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Modeling Wastewater Indicators and Effects of Contaminant Removal Strategies on Groundwater and Spring Discharge in a Karst Aquifer

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MODELING WASTEWATER INDICATORS AND EFFECTS OF CONTAMINANT REMOVAL STRATEGIES ON GROUNDWATER AND SPRING DISCHARGE IN A KARST AQUIFER

by

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ABSTRACT

This dissertation reports on research related to groundwater and contaminant transport to the Volusia Blue Spring (VBS), an Outstanding Florida Water Body located in Volusia County (Florida). The integration of springshed water quality and contaminant fate and transport (CFT) modeling played key roles in the evaluation of anthropogenic recharge impacts on VBS. To study anthropogenic recharge into the karst limestone aquifer, wastewater effluent, golf course ponds, septic tanks, groundwater monitoring wells, and VBS discharge were sampled for boron, nitrate-nitrogen, nitrate-oxygen and their isotopes spatially throughout the VBS springshed. Data related to natural water features, rainfall, land use, water use, treated wastewater discharge, and septic tank effluent flows was used as inputs to the three-dimensional CFT model developed from an integration of MODFLOW-2000 and MT3DMS. The model was calibrated and validated from field observed water levels and water quality taken throughout the springshed.

The purpose of this model is to understand groundwater and spring water quality throughout the VBS springshed. Water quality and model results indicate that water from the surficial aquifer in surrounding urban areas contributed to the flow and water quality at the spring's boil. Protection scenarios that included wetland treatment systems and the conversion of targeted septic systems to sewer were simulated to estimate future reductions of anthropogenic nutrients transported to the Spring. Of the scenarios evaluated in this study, targeted septic system removal results in the greatest benefit with a 36% nitrate decrease in a forty-year projection of spring discharge water quality. Results from this combined water quality and model development approach is expected to contribute an understanding of anthropogenic impacts from the urbanized developments overlying and surrounding the karst VBS aquifer.

This dissertation is dedicated to my children Evan and Lillian, who motivate me to live by faith, virtue, and excellence; and, to my husband Junos, who nourishes, energizes, and inspires me.

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I deeply appreciate the steady stream of support from my family. Mom and Dad always reminded me that at the end of the day everything would be alight. My daughter Lillian provided me an unlimited supply of you can do it's. My son Evan constantly reminded me that the extra work is worth the effort. My husband Junos made this entire endeavor possible, and he did so with unsurpassed humor, creativity, patience, and wisdom.

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LIST OF ABBREVIATIONS

CFT – contaminant fate and transport

FAS – Floridan Aquifer System

FDEP – Florida Department of Environmental Protection

FDOH – Florida Department of Health

LFA – Lower Floridan Aquifer

MGD – million gallons per day

ML – million liters

NMS – nitrogen management scenarios

NOAA – National Oceanic and Atmospheric Administration

OFW – Outstanding Florida Water

RMSE – root-mean-square-error

SJRWMD – St. Johns River Water Management District

TKN – total Kjeldahl nitrogen

TMDL – total maximum daily load

UFA – Upper Floridan Aquifer

VBS – Volusia Blue Spring

WWTF – wastewater treatment facility

CHAPTER ONE: GENERAL INTRODUCTION

Volusia Blue Spring (VBS) is classified as a first magnitude spring, meaning that it discharges more than 100 cubic feet per second (2.8 m^3/s) from the confining zone of the Floridan Aquifer System. The karst, urbanized springshed for Volusia Blue Spring (VBS) located in east central Florida was chosen as the study site because the primary nutrient sources (i.e. septic systems, wastewater treatment facilities, and fertilized areas) are characteristic of sources containing nitrogen and boron. In this dissertation, three-dimensional numerical contaminant fate and transport modeling utilizing boron and nitrate is employed to evaluate the impacts on groundwater quality from multiple sources including septic systems, treated wastewater discharges, and fertilizers. In consideration of the urbanized development surrounding the impaired waters of the VBS, an investigation into the contaminant transport patterns is needed for making decisions regarding groundwater movement, spring protection, and restoration.

The use of water quality and contaminant fate and transport modeling offered the ability to estimate the source of nutrient impacts to discharge and groundwater in the VBS springshed. The methods, results and evaluations of water quality and contaminant fate and transport modeling is described within Chapters Two through Five of this dissertation. The results of water quality taken from wastewater effluent, golf course ponds, groundwater monitoring wells, and VBS discharge is presented in Chapter Two. The water quality of septic tank supernatant is presented in Chapter Three. A conservative fate and transport model of anthropogenic boron in the VBS springshed is presented in Chapter Four. Finally, a reactive nitrate transport model including nitrogen management scenario analyses is presented in Chapter Five.

CHAPTER TWO: CHEMICAL AND ISOTOPIC CHARACTERIZATION OF A KARST, URBANIZED AQUIFER

Abstract

An urbanized development overlying a karst aquifer has been shown to contribute to the degradation of ecosystem quality by releasing anthropogenic solutes into groundwater systems. The complex nature of karst systems limits the ability to generalize fate and transport phenomena, however, chemical and isotopic composition of anthropogenic indicators is useful in this regard. To study anthropogenic recharge into a karst limestone aquifer, wastewater effluent, golf course ponds, septic tanks, groundwater monitoring wells, and a spring discharge were sampled for boron, nitrate-nitrogen, nitrate-oxygen and their isotopes spatially throughout a central Florida springshed. Unique boron isotopic signatures were found in treated wastewater (2.2–15.3‰), fertilizer (21.0‰), local limestone freshwater (40.0‰), and Volusia Blue Spring (VBS) discharge (28.4–45.9‰). Our findings indicate that VBS discharge is currently a varying mixture of limestone freshwater, relict seawater, and anthropogenic recharge.

Keywords: septic, anthropogenic, groundwater, fertilizer, boron, nitrate

Introduction

The Volusia Blue Spring (VBS) is located in a karst limestone springshed. This springshed was chosen as the study area because its discharge, the VBS, is downgradient of an urbanized area containing recharge from fertilized neighborhoods and golf courses, thousands of septic systems, and treated wastewater discharge (Figure 1). The VBS is classified as a first magnitude spring,

meaning that it discharges more than 100 ft^3/s (2.8 m^3/s) from the confining zone of the Upper Floridan aquifer (UFA). Located along the section of the St. Johns River located near Orange City, Florida, the VBS springshed is humid subtropical with a rainy season occurring between the months of May and October. According to the NOAA weather stations in Lisbon and DeLand, the mean annual rainfall between the years 1975 and 2015 was 1344 mm/year and temperatures near VBS varied from 5 to 33°F in 2014 (NOAA 2015).

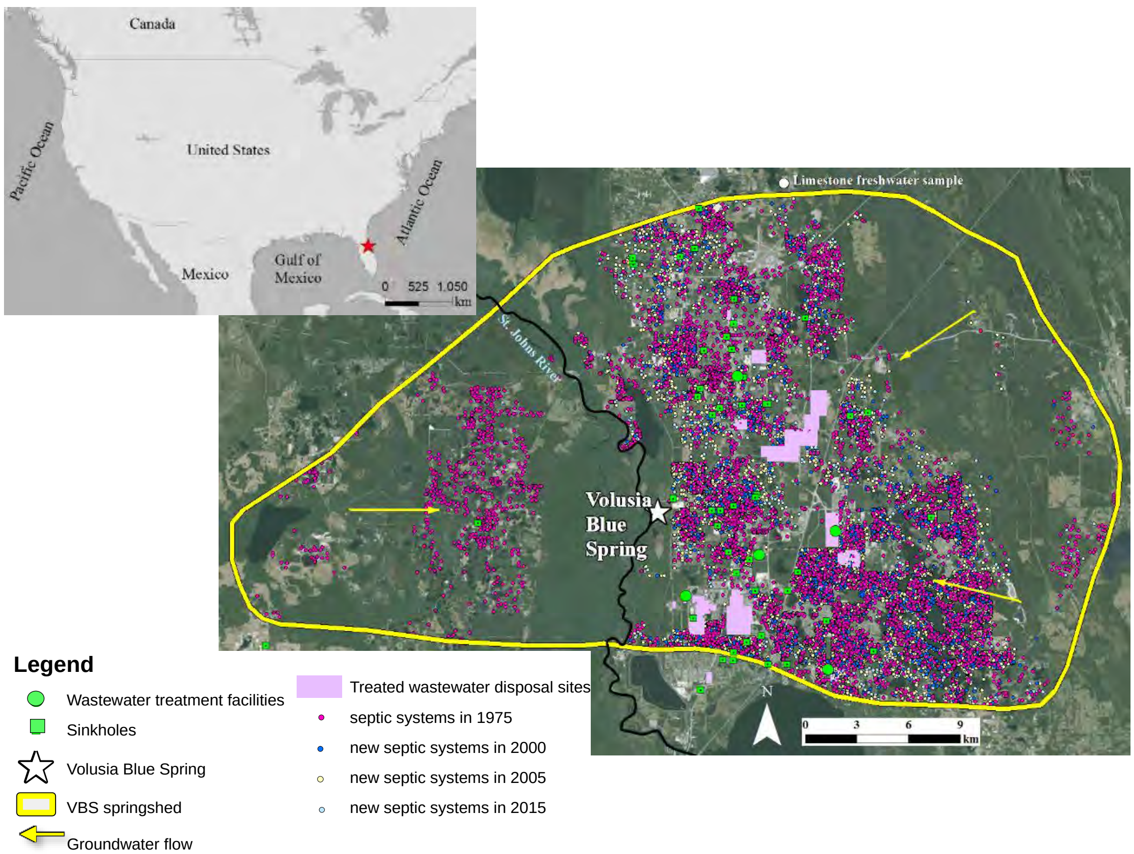

Figure 1: Location map of VBS showing the anthropogenic nutrient sources, groundwater flow direction, and sinkholes within its recharge area. Groundwater flow depicted from the VBS model (Reed, Wang, Duranceau 2016).

Within the VBS springshed, the primary sources of recharge include precipitation, treated wastewater, septic systems, and irrigation. The springshed contains more than 25,500 active septic

systems and five wastewater treatment facilities discharging more than 0.38 ML/d of treated wastewater (FDOH 2015; G. Robinson, SJRWMD, personal communication, 2015). Installation of septic system and treated wastewater discharges began prior to the 1970s and the 1990s, respectively, and have steadily increased since. In 2015, the VBS springshed received more than 16 ML/day of treated wastewater recharge (FDEP 2015) and more than 18 ML/day of septic system recharge (Roeder & Ursin 2013).

Nitrate concentrations in the discharge at VBS have steadily increased since 1976. In the years 1976 and 2009, the mean nitrate concentration at VBS was reported to be 0.12 and 0.72 mg/L, respectively (Holland & Bridger 2014). Because of the elevated nitrates observed at the spring, VBS became subject to regulations for a total maximum daily load (TMDL) for nutrients by the Florida Department of Environmental Protection (FDEP) in 2014 (Holland & Bridger 2014). Elevated nitrates observed in the ground- and surface waters within urbanized areas of France are shown to result from surrounding sewage effluents, fertilizers, and animal manure (Widory and colleagues 2004).

Previous water quality analyses shows anthropogenic influence in VBS discharge. Between 2012 and 2014, eight VBS discharge samples were found to contain, on average, 0.15 μg/L of sucralose (R. Hicks, FDEP, personal communication, 2015). Since sucralose is commonly used as an artificial sweetener, discharged in wastewater and septic systems, and conservative in the environment (Oppenheimer et al. 2011), its presence in VBS discharge is indicative of wastewater and groundwater assimilation.

In many parts of the world, considerable effort has been made to utilize nitrate isotopes for determination of anthropogenic mixing in groundwater (Aravena & Robertson 1998; Verstraeten et al., 2005; Widory et al. 2005), however, a degree of uncertainty exists when utilizing nitrogen

as a tracer because of processes such as denitrification, plant uptake, and/or soil retention (Leenhouts, Bassett & Maddock III 1998). Using bromide and chloride ratios, chlorides, vanadium, boron, and isotopes of boron, nitrogen, and oxygen, previous studies around the world indicate that other solutes may be useful in determining origins of anthropogenic nutrient sources (Verstraeten et al. 2005; Widory et al. 2004; Dickenson et al. 2011; Kamika & Momba 2012). In groundwater systems, Leenhouts, Bassett and Maddock III (1998) showed that boron is co-migratory to nitrate from source waters including wastewater and agricultural flows.

The purpose of this study was to characterize the VBS discharge and the prospective nutrient sources that impact its water quality. Previous studies have utilized isotopic boron to characterize groundwater and potential nutrient endmembers such as agriculture, wastewater, and fertilizers (Barth 1998; Bassett 1995; Leenhouts, Bassett & Maddock III 1998; Vengosh 1994). In their study, Leenhouts, Bassett and Maddock III (1998) compared ion concentrations and tri-linear plots to boron isotopic plots and found that isotopic boron plots provided superior distinction between sources of nitrogen that included agriculture and municipal wastewater. In this study, mixing limits are indicated by isotopic boron plots and confirmed by plots of inorganic and boron concentrations of waters from the VBS springhsed. A boron transport model of VBS springshed was produced by Reed and Duranceau (2016). Results of their study indicate that in the year 2015, boron from septic systems was mixed with VBS discharge, however, treated wastewater discharge had not yet reached VBS. Results of the chemical and isotopic characterization of groundwater and endmembers in this study will serve to either confirm or refute modeled results from Reed and Duranceau (2016).

A water quality anthropogenic nutrient impact study of the VBS springshed has not been published. The availability of endmember (septic tanks, treated wastewater, and fertilizers) and

spring discharge characterization within the VBS springshed is lacking, if non-existent; consequently, the evaluation of chemical and isotopic characterizations of the springshed would contribute to the greater body of knowledge in regards to the management of spring water quality. In consideration of the urbanized development surrounding the impaired waters of the VBS, investigation into the origin of anthropogenic presence at VBS is needed for making decisions on groundwater and spring protection restoration strategies.

Hydrogeology

Groundwater flows towards VBS as indicated by the flow arrows shown in Figure 1. Characteristic of karst aquifers, particularly the aquifer of VBS, is the sinkhole areas that provide rapid infiltration by direct connections between the surficial and underlying confined aquifers (Ravbar & Goldscheider 2009). The Florida Geological Survey (2015) reports that there are more than forty subsidence incidents, commonly known as sinkholes in the karst VBS recharge area (Figure 1). An age-dating tracer study using chlorofluorocarbon CFC-113, tritium, helium-3, and sulfur hexafluoride by Toth and Katz (2006) found that spring water at VBS is more than thirty years of age.

The groundwater system within the VBS recharge area consists of an unconfined surficial aquifer and the confined Floridan Aquifer System (FAS). According to Toth and Katz (2006), the surficial aquifer in proximity of the VBS is underlain by well-drained Holocene and Pleistocen sand, sandy silt and clay that form the intermediate confining unit. Studies indicate that boron presence in the FAS below the St. Johns River may be the influence of relict seawater (Mercer et al. 1986; SJRWMD 2011; Weast et al. 1985). From the tri-linear plot (Figure 2) of VBS discharge and water collected from the local freshwater well location, there is indication that VBS discharge

originates from an aquifer composed of seawater, calcite, and dolomite. As evidenced by elevated chlorides thought to have been enabled by groundwater circulation patterns and soil adsorption, the SJRWMD (2011) reported the presence of relict seawater in the confining zones of the St. Johns River and VBS. Although discussion of boron was not included, seawater contains, on average, 4.5 mg/L total boron and an isotopic boron signature of 40‰ (Foster, Pogge von Strandmann & Rae 2010; Weast et al. 1985).

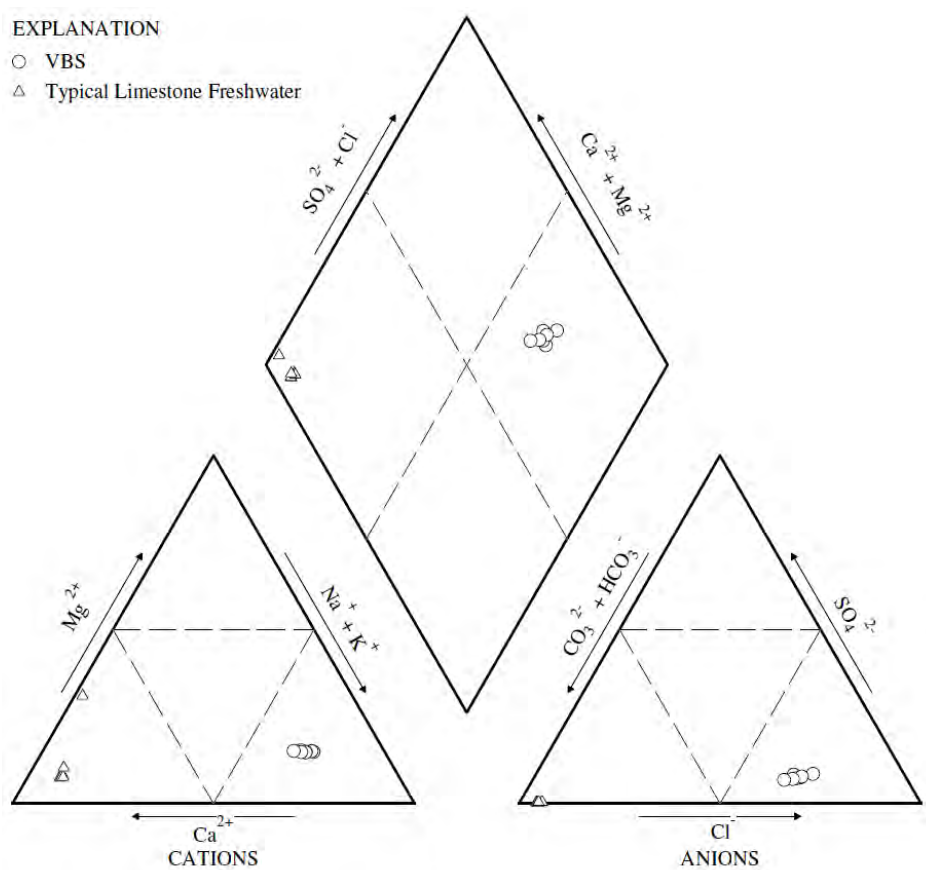

Figure 2: Tri-linear plot of VBS discharge and limestone freshwater well. Data obtained from SJRWMD Webapub (2015).

Methods

Groundwater sampling included the collection of VBS discharge and water from the upper Floridan and surficial aquifers throughout the springshed. Nineteen VBS discharge samples, twelve UFA samples, and five surficial aquifer samples were collected between April and November, 2015. VBS discharge samples were collected above the boil, 8 inches below the water surface. UFA and surficial aquifer samples were collected from monitoring wells located throughout the springshed. Groundwater samples were analyzed for boron and nitrate, and isotopic analysis was performed on one UFA and three VBS discharge samples.

Endmember sampling included the collection of limestone freshwater, treated wastewater, septic tank supernatant, fertilized areas, and fertilizer for nitrogen and boron analysis. Two limestone freshwater samples were collected from a monitoring well located within the confined upper Floridan aquifer (see Figure 1). A total of five treated wastewater and twenty-four septic tank supernatant (Reed & Duranceau 2016) were collected between April and December, 2015. Wastewater effluent samples were collected just after disinfection. Fertilizers are represented by samples obtained from monitoring wells at golf course locations. In addition, an unknown fertilizer sample collected from a golf course within the VBS springshed was dissolved, extracted, filtered (0.45-µm) and analyzed for chemical and isotopic composition. Isotopic analysis was performed on three treated wastewater and five septic tank supernatant samples (Reed & Duranceau 2016).

Samples for nitrate were collected and stored at $4^{0}C$. Samples for total boron and TKN analysis were collected in nalgene bottles that were rinsed with deionized-distilled water, and acidified to pH 2 with HNO_3 or H_2SO_4, respectively, and stored at $4^{0}C$. Isotope samples were collected and stored in rinsed nalgene bottles, filtered through 0.45-µm filters, and stored frozen.

Table 1: Summary of water quality method analysis

Compound	Method	Reference
Nitrate	Ion-exchange chromatography spectroscopy (IC); EPA Method 300.0	USEPA 1993a
total Kjeldahl nitrogen	Semi-automated colorimetry; EPA Method 351.2	USEPA 1993b
Total boron	Inductively coupled plasma mass spectrometry (ICP-MS); EPA Method 200.7	USEPA 2001
Boron isotope	Thermal ionization mass spectrometer	Hemming & Hanson 1994
Nitrate isotope	Isotope ratio mass spectrometer (IRMS)	USGS 2012

Samples analyzed for pH, conductivity, temperature, turbidity, and dissolved oxygen by use of a Hach HQ40d portable multi-parameter meter. A list of measured compounds and analytical methods used is available in Table 1. Nitrate, TKN, and total boron concentrations were determined at the Advanced Environmental Laboratories, Inc. in Tampa, Florida. Nitrate concentrations were determined by ion chromatography (Dionex ICS-1000). TKN was determined by semi-automated colorimetry (SEAL Analytical QuAAtro39) in which biological nitrogen components were converted to ammonia through a copper sulfate digestion. Total boron concentrations were made on a Perkin Elmer inductively coupled plasma mass spectrometry Optima 5300 DV with detection limits ranging from 0.005 to 0.03 mg L^{-1}.

Boron isotopic measurements were made at the Tetra-Tech, Inc. Boron Isotope Laboratory (Fort Collins, CO) on a thermal ionization mass spectrometer, TIMS VG 336, built by VG Isotopes Limited, Cheshire, England. The analytical method uses the internationally accepted boric acid standard with an isotopic ratio for $^{11}B/^{10}B$ of 4.04362 +/- 0.00137 (2σ) in positive ion mode or $^{11}B/^{10}B$ of 4.0014 +/- 0.0027 (2σ) in negative ion mode (Hemming & Hanson 1994). The standard deviation from analyses of the NBS SRM 951 standard was less than ± 1.00‰ $\delta^{11}B$.

Nitrate-nitrogen and nitrate-oxygen isotopic measurements were made at Northern Arizona University's Colorado Plateau Stable Isotope Laboratory on an IRMS, Thermo-Quest Delta Plus, built by Thermo Finnigan LLC. The "denitrifier method" was used to reduce nitrate for analysis by IRMS. The standard deviation from analyses of the internationally accepted standard was less than 0.30‰ for $\delta^{15}N$ (1σ) and less than 0.60 for $\delta^{18}O$ (1σ) for samples with nitrate concentrations greater than 0.07 mg L^{-1}.

Results and discussion

Chemical parameters

Nitrate, boron, and chloride concentrations were evaluated in endmembers and VBS discharge waters. Endmembers included anthropogenic nutrient sources and a local limestone freshwater sample located near the springshed boundary and more than 400 meters from a septic system. Nitrogen and boron were analyzed in samples collected directly from septic tanks and wastewater treatment facilities within the VBS springshed. Results show that treated wastewater effluent contains the highest level of boron; whereas, septic tanks contain the highest level of nitrogen (Table 2). According to anthropogenic nitrate and chloride plots presented in Figure 3, anthropogenic endmember assimilation appears to occur in VBS discharge. A plot of nitrate versus boron (Figure 3a) and chloride versus boron (Figure 3b) both indicate VBS discharge is influenced by septic systems.

Table 2: Water quality of anthropogenic endmembers and VBS discharge.

Statistical parameter	Treated wastewater effluent			Septic tank supernatant			VBS discharge			Fertilized areas	
	Nitrate (mg/L)	Boron (mg/L)	Chloride [1] (mg/L)	TKN[2] (mg/L)	Boron (mg/L)	Chloride [3] (mg/L)	Nitrate (mg/L)	Boron (mg/L)	Chloride [4] (mg/L)	Nitrate (mg/L)	Boron (mg/L)
Number of samples	5	9	622	15	23	4	18	19	39	2	2
Minimum	0.5	0.170	11	2.8	0.029	27	0.15	0.110	11	1.2	0.032
Maximum	7.1	0.230	230	93.0	0.180	41	1.2	0.130	567	14	0.038
Mean	3.8	0.20	75	48.9	0.09	35	0.8	0.11	341	7.6	0.04
Standard deviation	2.7	0.02	38.7	27	0.04	5.0	0.3	0.01	120	6.4	0.003

[1]Represents 2005 through 2014 chloride data retrieved from a treatment facility located within the VBS springshed (FDEP 2015)

[2]Literature indicates that septic tank effluent, which contains nitrogen mostly in the form of TKN, enters the environment via drainfields and groundwater in which nearly all the TKN is converted to NO_3-N (Katz et al. 2010)

[3](Katz et al. 2010)

[4]Represents 2002 through 2011 chloride data retrieved from the VBS vent (SJRWMD Webapub 2015)

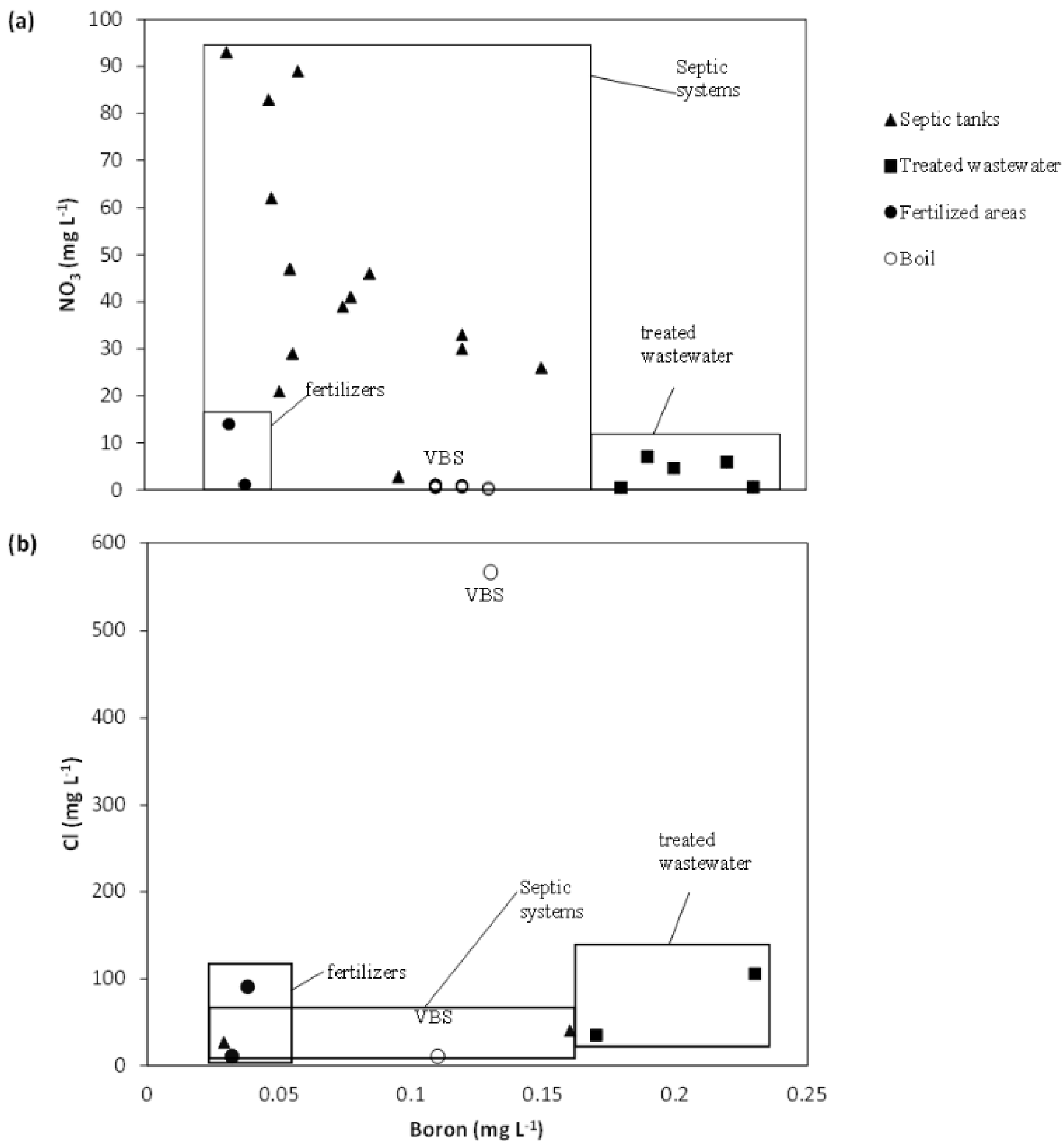

Figure 3: Mixing scenarios from plots of nitrate and chloride versus boron indicating VBS discharge contains influences from septic systems and fertilizers. Chloride vs. boron is represented as ranges of maximum and minimum chloride and boron concentrations. Chloride data was obtained from literature (FDEP 2015; Katz et al. 2010; SJRWMD Webapub 2015)

Isotopic composition

Toth and Katz (2006) estimate that VBS discharge is more than thirty years of age. The boron transport model of VBS (Reed, Wang, & Duranceau 2016) indicates that anthropogenic boron from treated wastewater discharges and fertilizers has not yet reached VBS. From Figure 4, waters with similar concentrations of boron have different isotopic signatures. Mixing lines 1 and 2 show that septic tanks and treated wastewater discharges, respectively, currently influence the boron isotopic value of VBS discharge. However, from the data presented in Figure 4, it appears that fertilizers do not currently have an effect on $\delta^{11}B$ values in VBS discharge. The third mixing line shown in the boron isotopic plot (Figure 4) does support previous literature findings that indicate the presence of relict seawater in the FAS near VBS (Mercer et al. 1986; SJRWMD 2011; Weast et al. 1985); where seawater is known to contain up to 4.5 mg/L of boron (Weast et al. 1985) and average $\delta^{11}B$ values of 39.61‰ (Foster, Pogge von Strandmann, and Rae 2010).

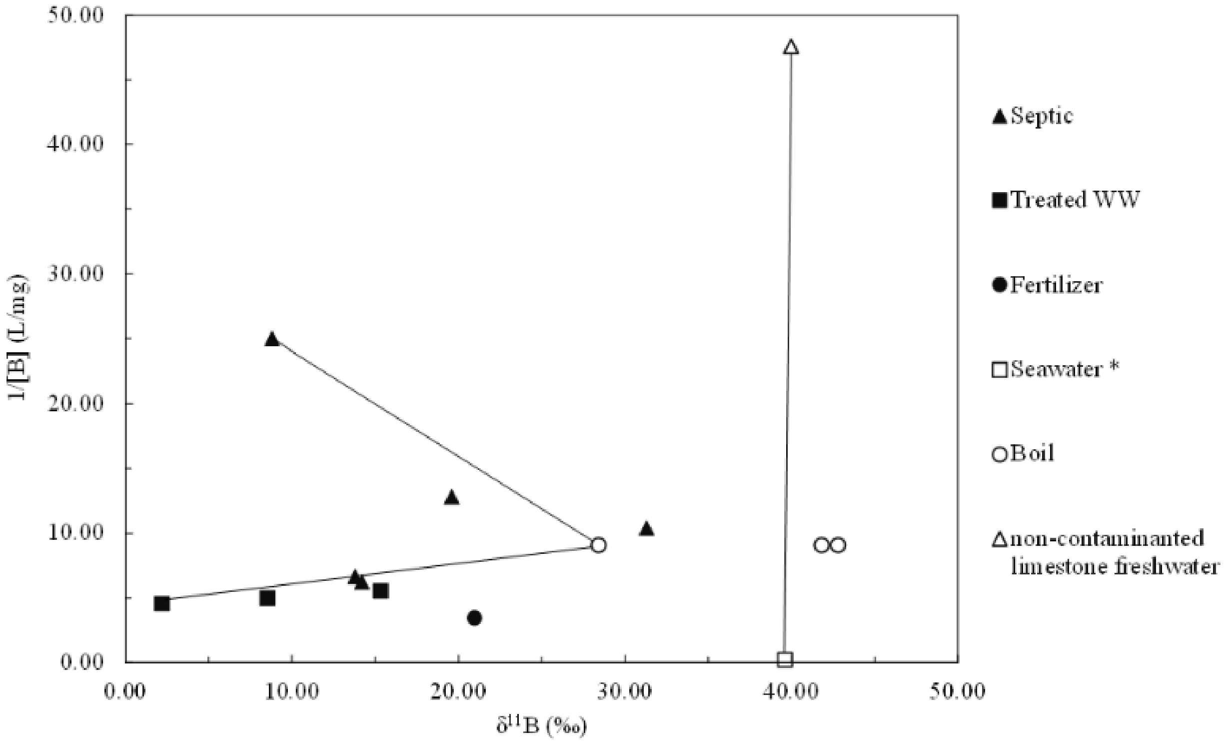

Figure 4: Boron isotopic plot indicating the boron isotopic signature of VBS discharge contains influences of septic tanks, treated wastewater, relict seawater, and limestone freshwater.

The three boron isotopic signatures of VBS do have a larger than expected range of values. It should be noted that the lowest boron isotopic signature observed in VBS discharge represents a discharge sample collected in April 2015, just before the rainy season typically occurs. The other two VBS discharge samples of higher isotopic value were collected in August 2015, towards the end of the rainy season.

Conclusions

The objective of this study was to characterize VBS discharge and endmembers that are likely to contribute to the excessive nitrate concentrations observed at VBS. Endmembers included seawater, typical limestone freshwater, treated wastewater discharges, septic systems, and

fertilizers. Isotopic boron signatures were found in treated wastewater (2.2–15.3‰), fertilizer (21.0‰), local limestone freshwater (40.0‰), and Volusia Blue Spring (VBS) discharge (28.4–45.9‰). From the results of this study, it can be implied that the anthropogenic boron and nitrate in the spring's vent in the year 2015 is caused primarily by septic systems with some treated wastewater influence. Based on the results of this study, the urbanized areas served by septic systems impairs Volusia Blue Spring and should be evaluated for improvement so that groundwater protection strategies can be implemented.

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CHAPTER THREE: CHEMICAL AND ISOTOPIC COMPOSITION OF SEPTIC TANK SUPERNATANT

Abstract

Most of earth's population depends on onsite sewage systems to dispose of their wastewater to the environment, degrading ecosystem quality. Samples used to estimate contaminant transport in the environment, however, have typically been collected from sources external to the septic tank. Here we characterize for the first time the isotopes of boron, nitrate-nitrogen and nitrate-oxygen in supernatant collected directly from within septic tanks located in a karst limestone springshed. Among other parameters, total Kjeldahl nitrogen (TKN) and total boron were also evaluated. Nitrate-nitrogen isotopes ranged from +1.25‰ to +10.00‰ and boron isotopic signatures ranged from +8.8‰ to +31.3‰. Nitrate-oxygen isotopes ranged from -3.23‰ to +19.96‰ and were indicative of an anoxic environment. On average, residential septic tanks were found to contain 96 µg L^{-1} total boron and 63 mg L^{-1} TKN. Our findings show that septic tanks directly contribute anthropogenic boron to the environment at greater amounts than previously assumed.

Keywords: boron, karst, onsite sewage, total Kjeldahl nitrogen, pollution

Main

Up to eighty-five percent of any country's population depend on septic or other types of onsite systems to dispose of their wastewater (The World Bank, 2013); in North America this number drops to approximately twenty-five percent (Alhajjar, Chesters & Harkin, 1990). Primarily due to nutrient loadings, this method of disposal impacts the environment (Katz & Griffin, 2008;

Landon et al., 2008; McQuillan, 2004; Silva et al., 2002; Verstraeten et al., 2005). It is commonly accepted that septic tanks contain nitrogen-based nutrients (Charles et al., 2005; Widory et al., 2005), however, their impact to groundwater systems has been based on estimated or assumed geochemical reaction rates (Cabrera, 1993; Conan et al., 2003; Postma & Boesen, 1991). Because geochemical reaction rates are subject to competing effects, their use in monitoring the transport of contaminants in alluvial karstic systems is suspect; hence, other means for contaminant transport characterization are under investigation and have recently focused on boron (Katz & Griffin, 2008; Landon et al., 2008; Verstraeten et al., 2005). Despite the impact that septic tanks have on the environment, supernatant is not typically sampled for quality, as surrogate samples are collected from outside the limits of the septic tank or within the adjacent drainfield (Katz et al., 2010; Pradhan et al., 2011).

The use of conservative indicators, such as boron, has hence gained attraction for use as a marker in many aquatic environments (Benson et al., 1991), a co-migrant to nitrogen from wastewater sources (Seiler, 2005), and a tracer for treated wastewater discharge (Barber et al., 2998; Leenhouts, Basset, Maddox III, 1998; Vengosh et al., 1994). Boron at concentrations between 10 and 200 $\mu g\ L^{-1}$ can either stimulate or inhibit algal growth, depending on the species (Forsberg, Jinnerot, Davidsson, 1967). In agriculture, high concentrations of boron can be toxic particularly to fruit and nut trees (Gupta, 1993).

Boron and its isotope have not been reported in septic tank supernatant because active septic tanks are hazardous and difficult to access. Consequently, as is the case with geochemical reaction rates, assumptions or surrogate methods are used to estimate septic tank contributions to the environment. Others (Katz & Griffin, 2008; Landon et al., 2008) have reported that groundwater near septic tanks contains between 36 and 290 $\mu g\ L^{-1}$ of total boron; however, isotopic

content was not reported. Although Verstraeten and colleagues (2005) estimated that groundwater in proximity of septic tanks contained between -0.2 to +14.5‰ of isotopic boron, septic tanks had not been sampled. Many correlate septic tank contributions to the environment by assuming wastewater discharges contain similar conservative or non-reactive solutes (Saccon et al., 2013; Widory et al., 2005), however, septic tank supernatant solute content is not used to verify the accuracy of the correlation. Others have attempted to use nitrogen, phosphorus, and chlorides (Alhajjar, Chesters & Harkin, 1990; Charles et al., 2005) to serve as a surrogate for septic tank contributions to the environment; however, these methods are suspect due to exchange, adsorption and biological uptake.

Here, we gained access to twenty-four private residential septic tanks for water quality sampling purposes. The characterization and presence of chemical and isotopic parameters in septic tanks is expected to enhance our understanding of septic supernatant impacts on groundwater systems in which nitrogen and boron co-migrate. The availability of actual septic tank isotopic water quality information is lacking, if non-existent; consequently, any vetted data that could be published and made readily available would contribute to the greater body of knowledge in this regard. We report for the first time the results of septic tank supernatant sampling for total Kjeldahl nitrogen (TKN), boron, and isotopes of boron, nitrate-nitrogen and nitrate-oxygen nitrate.

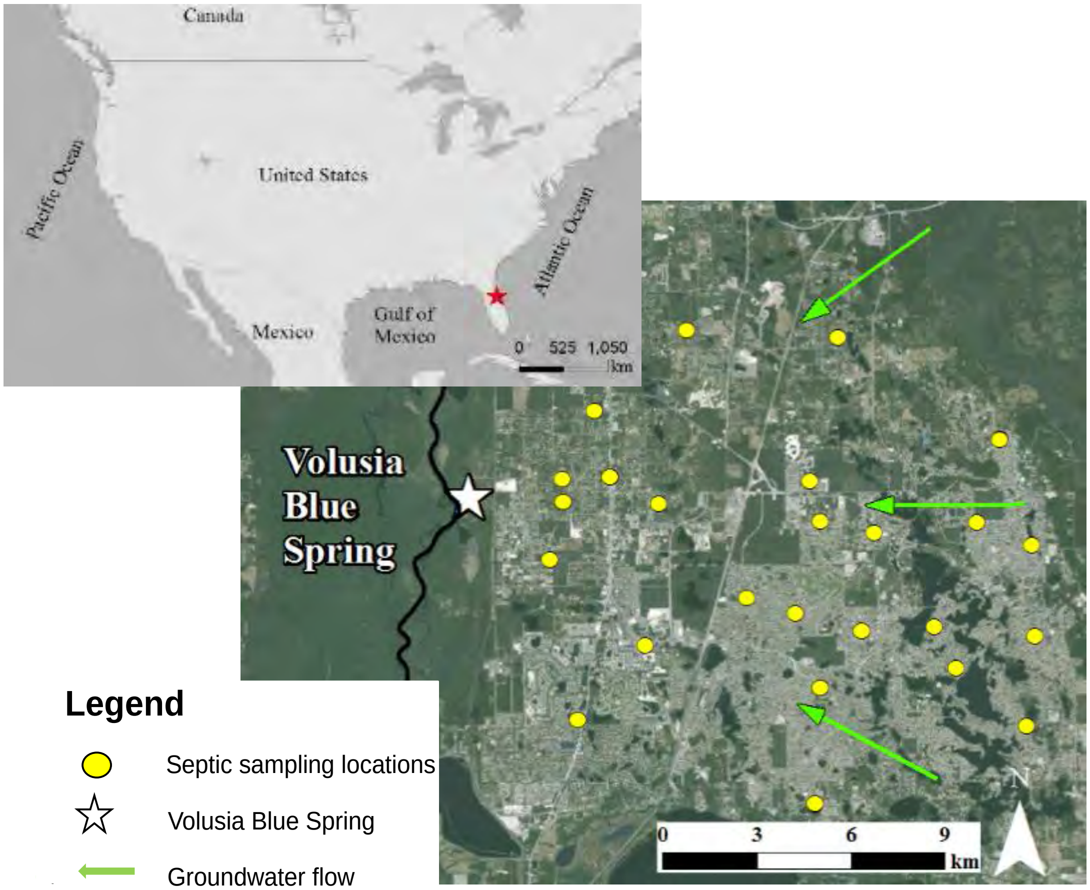

Figure 5: Location map of the septic tank sampling locations within the Volusia Blue Spring springshed

The Volusia Blue Spring springshed is located in central Florida, United States (Figure 5). This springshed shows great ecological and economical importance because, like many others throughout the world, it is a drinking water source for many (SJRWMD, 2006). It was chosen as the study area because this first magnitude spring, surrounded by tens of thousands of septic systems (FDOH, 2015), is refuge for hundreds of manatees during winter months. Associated with these septic systems is the movement of untreated wastewater from anaerobic septic tanks towards aerobic drainfields where percolation into unsaturated soils and transport into groundwater occurs.

Methods

A total of twenty-four septic tank supernatant samples were collected throughout the springshed between April and December, 2015. Samples of supernatant were collected between 5 cm and 10 cm underneath the water surface (supernatant) within the septic tank. In many cases, sweeping the top prior to sampling was required to obtain samples free of sludge and scum. Samples for nitrate were collected and stored at 4^{0}C. Samples for total boron and TKN analysis were collected in nalgene bottles that were rinsed with deionized-distilled water, and acidified to pH 2 with HNO_3 or H_2SO_4, respectively, and stored at 4^{0}C. Isotope samples were collected and stored in rinsed nalgene bottles, filtered through 0.45-µm filters, and stored frozen.

Table 3: Summary of water quality method analysis

Compound	Method	Reference
Nitrate	Ion-exchange chromatography spectroscopy (IC); EPA Method 300.0	USEPA, 1993a
total Kjeldahl nitrogen	Semi-automated colorimetry; EPA Method 351.2	USEPA, 1993b
Total boron	Inductively coupled plasma mass spectrometry (ICP-MS); EPA Method 200.7	USEPA, 2001
Boron isotope	Thermal ionization mass spectrometer	Hemming & Hanson, 1994
Nitrate isotope	Isotope ratio mass spectrometer (IRMS)	USGS, 2012

Supernatant was analyzed for pH, conductivity, temperature, turbidity, and dissolved oxygen using a Hach HQ40d portable multi-parameter meter. A list of measured compounds and analytical methods used is available in Table 3. Nitrate, TKN, and total boron concentrations were determined at the Advanced Environmental Laboratories, Inc. in Tampa, Florida. Nitrate concentrations were determined by ion chromatography (Dionex ICS-1000). TKN was determined

by semi-automated colorimetry (SEAL Analytical QuAAtro39) in which biological nitrogen components were converted to ammonia through a copper sulfate digestion. Total boron concentrations were made on a Perkin Elmer inductively coupled plasma mass spectrometry Optima 5300 DV with detection limits ranging from 0.005 to 0.03 mg L^{-1}.

Boron isotopic measurements were made at the Tetra-Tech, Inc. Boron Isotope Laboratory (Fort Collins, CO) on a thermal ionization mass spectrometer, TIMS VG 336, built by VG Isotopes Limited, Cheshire, England. The analytical method uses the internationally accepted boric acid standard with an isotopic ratio for $^{11}B/^{10}B$ of 4.04362 +/- 0.00137 (2σ) in positive ion mode or $^{11}B/^{10}B$ of 4.0014 +/- 0.0027 (2σ) in negative ion mode (Hemming & Hanson, 1994). The standard deviation from analyses of the NBS SRM 951 standard was less than +/- 1.00‰ $\delta^{11}B$.

Nitrate-nitrogen and nitrate-oxygen isotopic measurements were made at Northern Arizona University's Colorado Plateau Stable Isotope Laboratory on an IRMS, Thermo-Quest Delta Plus, built by Thermo Finnigan LLC. The "denitrifier method" was used to reduce nitrate for analysis by IRMS. The standard deviation from analyses of the internationally accepted standard was less than 0.30‰ for $\delta^{15}N$ (1σ) and less than 0.60 for $\delta^{18}O$ (1σ) for samples with nitrate concentrations greater than 0.07 mg L^{-1}.

Results and Discussion

Literature indicates that septic tank effluent, which contains nitrogen mostly in the form of TKN, enters the environment via drainfields and groundwater in which most of the TKN is converted to NO_3-N (Katz et al., 2010). Co-migrant to nitrogen in wastewater is boron, which is conservative in many aquatic and alluvial systems (Bassett et al., 1995; Saccon et al., 2013; Seiler,

2005). At the observed pH range (Table 4), boron in septic tanks is in the form of the uncharged boric acid, thus discharge to alkaline groundwaters may affect the speciation of boron.

Table 4: Summary of water quality of septic tank supernatant.

Statistical parameter	pH	Specific conductance (µS/cm)	Temperature (^{0}C)	Turbidity (NTU)	Dissolved O_2 (mg/L)
Minimum	6.2	582	24	10	0.07
Maximum	7.5	1568	30.1	918	2.36
Mean	6.7	1161	27.4	72.8	0.73
Standard Deviation	0.3	265	1.8	296	0.8

Septic tank supernatant samples were analyzed for nitrate but were below detection limits (< 0.051 mg L^{-1}); however, TKN and boron were present in each sample analyzed (Figure 6a). Total boron concentrations in septic tanks are skewed towards the upper range, as indicated by the length of the top whisker of the boron plot in Figure 7; whereas the TKN plot shows a relatively even distribution of data. The presence of boron in septic tanks varies, seemingly as a result of homeowners' product use practice. Boron is a whitening agent in many household cleaning products, but if the homeowner does not use these products, total boron concentrations may be low, while TKN values may be relatively high.

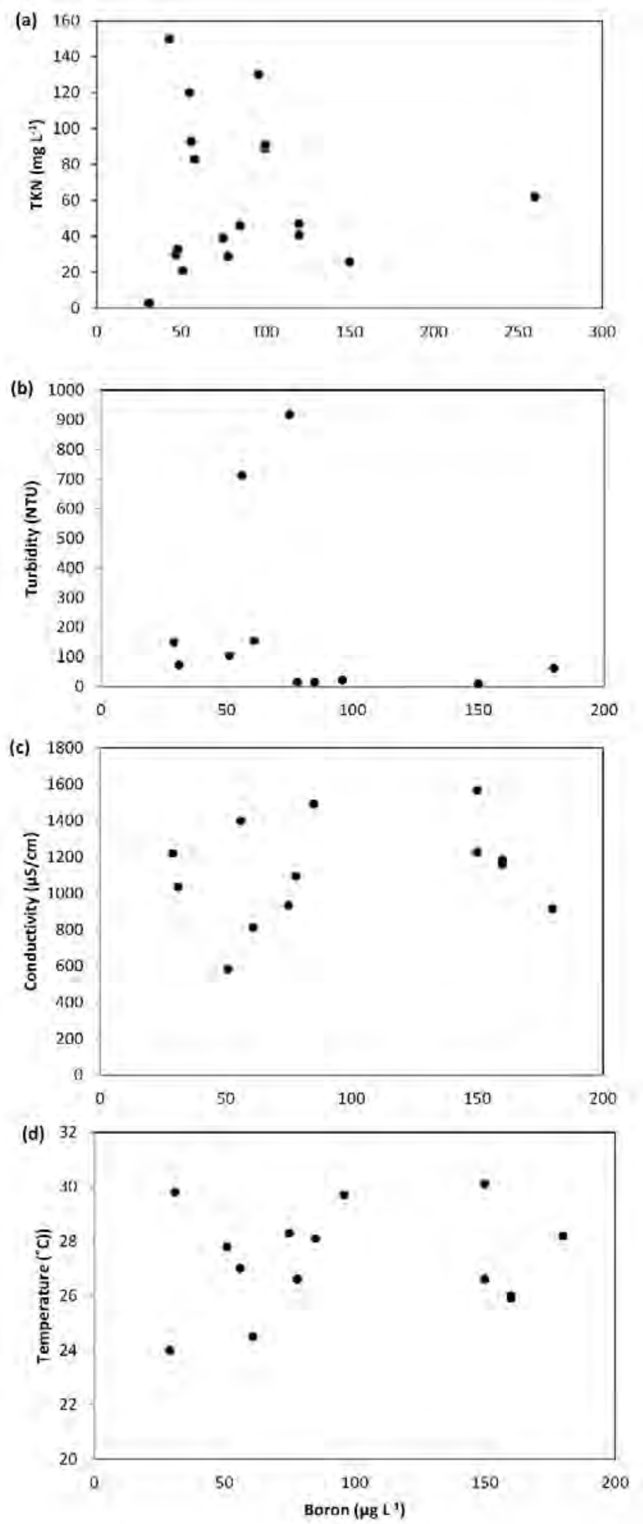

Figure 6: Boron non-correlation plots of a) TKN; b) turbidity; c) conductivity; d) temperature vs. total boron in septic tanks.

On average, the supernatant of septic tanks contained total boron and TKN concentrations of 96 μg L^{-1} and 63 mg L^{-1}, respectively. Although the highest concentration of total boron detected in the twenty-four septic tanks was 260 μg L^{-1}, the overall range of observed total boron in septic tanks (29 to 260 μg L^{-1}) is consistent with literature findings of total boron in groundwater near septic tanks, ranging from 36 to 290 μg L^{-1} (Katz & Griffin, 2008; Landon et al., 2008). Considering the consistency of boron levels in septic tanks and groundwater, the data obtained from septic tank supernatant supports the assumption that total boron and nitrogen co-migrate from septic tanks to nearby groundwater (Katz & Griffin, 2008; Seiler, 2005).

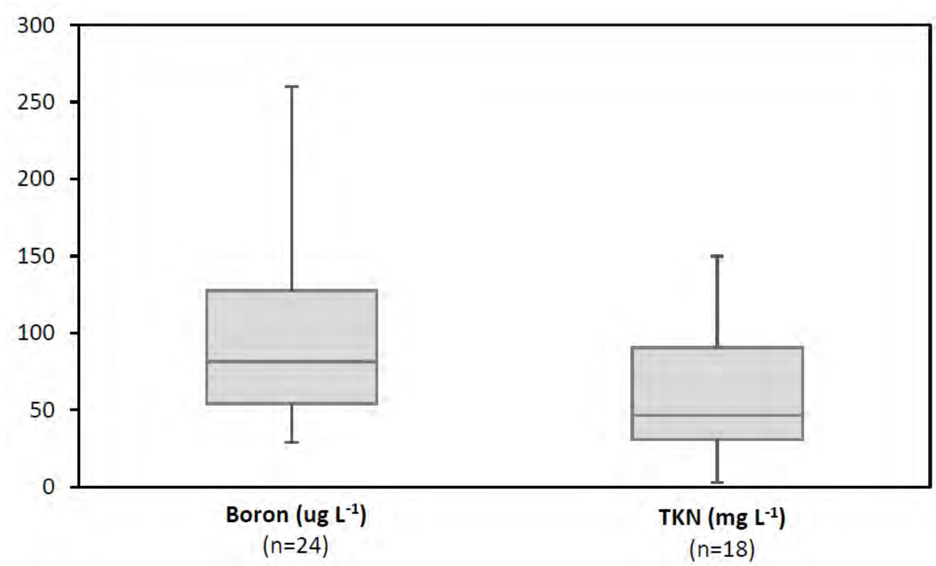

Figure 7: Box and whisker plots of boron and TKN in septic tanks. The middle line in each box represents the median of the data and the lower and upper lines of each box indicate the lower and upper quartiles, respectively. Maximum and minimum values are represented by the whisker lines extending from each box.

The septic tanks that were sampled for boron isotopes range from +8.8‰ to +31.3‰ (Figure 8). Since boron is conservative in most aquatic and alluvial systems and unaffected by biological wastewater treatment (Bassett et al., 1995; Saccon et al., 2013; Widory et al., 2005), it

was expected that the isotopic signature of septic tank supernatant would closely resemble domestic wastewater and groundwater near septic tanks. However, the $\delta^{11}B$ values in septic tank supernatant range higher than both treated domestic wastewater (Saccon et al., 2013; Widory et al., 2005) and groundwater near septic tanks (Verstraeten et al., 2005). Varied isotopic values of similar waters may be indicative of source mixing (Bassett et al., 1995), however the boron isotopic signature of other sources, such as native groundwater, in this study area is unknown.

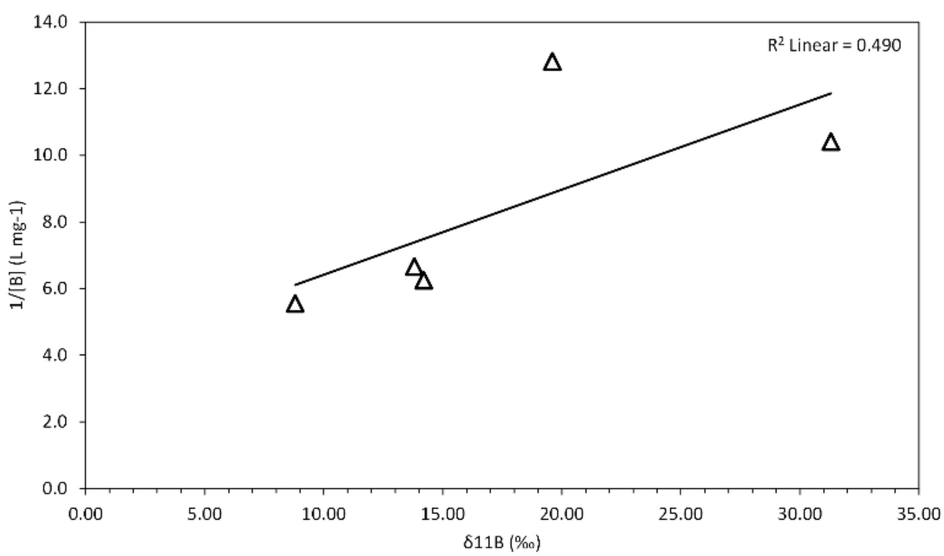

Figure 8: Boron isotopic signature of septic tank supernatant.

Nitrate isotopes from three septic tanks sampled were analyzed for determination of nitrate-nitrogen and nitrate-oxygen isotopic signatures. N-isotope ratios in septic tanks ranged from +1.25‰ to +10.00‰, while $\delta^{18}O$ ratios ranged from -3.23‰ to +19.96‰. N-isotope ratios from our study yield a lower range than with data from literature measured on sewage outputs (Saccon et al., 2013; Widory et al., 2005). However, concentrations of nitrate were below laboratory method detection levels (0.05 mg L^{-1}), therefore, precision may have been affected.

Conclusion

This is the first study that characterized TKN as well as nitrate, boron, oxygen and their respective isotopic content in septic tanks; consequently, the characterization of these water quality parameters in septic tanks enhances our understanding of supernatant contents that contribute to groundwater systems in which nitrogen and boron co-migrate. The presence of boron and TKN in septic tank supernatant confirms previous assumptions that boron and nitrogen co-migrate; however, the variability in the TKN and boron data show that a direct correlation cannot be made. This research has shown that the chemical and isotopic content of septic tank supernatant discharge directly contributes anthropogenic boron and nitrogen to the environment.

Acknowledgments

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CHAPTER FOUR: MODELING ANTHROPOGENIC BORON IN GROUNDWATER FLOW AND DISCHARGE AT VOLUSIA BLUE SPRING (FLORIDA, U.S.)

Abstract

Volusia Blue Spring (VBS) is the largest spring along the St. Johns River in Florida and is refuge for hundreds of manatees during winter months. However, the water quality of the spring flow has been degraded due to urbanization in the past decades. In this paper, a three-dimensional contaminant fate and transport model, utilizing MODFLOW-2000 and MT3DMS, was developed to simulate boron transport in the Upper Florida Aquifer, which sustains the VBS spring discharge. The VBS model relied on information and data related to natural water features, rainfall, land use, water use, treated wastewater discharge, septic tank effluent flows, and fertilizers as inputs to simulate boron transport. The model was calibrated against field observed water levels, spring discharge, and field observed boron. The calibrated VBS model yielded a root-mean-square-error value of 1.8 m for head and 17.7 μg/L for boron concentrations within the springshed. Model results show anthropogenic boron from surrounding urbanized areas contributes to the boron in the spring's vent.

Keywords: karst, solute transport, anthropogenic boron, MODFLOW, MT3D

Introduction

Agricultural practices and wastewater effluent in springsheds produce significant concentrations of nitrate and boron in groundwater systems and spring discharge (Chetelat &

Gaillardet 2005; Hasenmueller & Criss 2013; Widory et al. 2005). Nitrate is of particular concern in many groundwater systems because its elevated presence is known to stimulate algal growth (Stevenson et al. 2007) and possibly decline diversity and productivity of plants in spring runs (Holland & Bridger 2014). Boron at concentrations between 10 and 200 µg/L can either stimulate or inhibit algal growth, depending on the species (Forsberg and colleagues 1967). In agriculture, high concentrations of boron can be toxic particularly to fruit and nut trees (Gupta 1993). In groundwater systems, Leenhouts et al. (1998) showed that boron is co-migratory to nitrate from source waters including municipal wastewater and agricultural flows.

Contaminant fate and transport (CFT) models have been developed to investigate the transport phenomena of nitrogen in aquifers (Almasri & Kaluarachchi 2005; Conan et al. 2003). Observations of contaminant concentration and quantification of aquifer recharge are critical inputs to CFT models (Almasri & Kaluarachchi 2007). Postma (1991) used PHREEQM to model the contaminant transport of nitrate. Refsgaard et al. (1991) applied a soil nitrate dynamic transformation model to determine contaminant concentration leaching to groundwater. The integration of MODFLOW (Harbaugh et al. 2000) and MT3DMS (Zheng & Wang 1999) is a popular modeling tool for simulating the transport of solutes for surface water into the subsurface as well as identifying percentages of surface water present in the subsurface (Conan et al. 2003; Lautz & Siegel 2006; Prommer et al. 2003). Using MT3D, Almasri and Kaluarachchi (2005) developed a three-dimensional nitrate fate and transport model of the Sumas-Blaine aquifer in an agricultural area of Washington State. This model relied on estimates of reaction rates, advection, and dispersion to predict the fate and transport of nitrogen from agricultural sources within the basin.

Modeling nitrate sources in groundwater requires the accurate estimation of reactions, advection and dispersion of reactive tracers (Yeh & Tripathi 1989), such as nitrate, or the utilization of co-migratory conservative tracers that do not geochemically react. Nitrate is subject to geochemical reactions that alter its oxidation state, so a degree of uncertainty exists when estimating nitrate fate and transport because of processes such as denitrification, plant uptake, and/or soil retention (Leenhouts et al. 1998). However, Leenhouts et al. (1998) showed that boron is resistant to oxidation/reduction reactions and biological transformations in aqueous solutions and is, therefore, a suitable conservative tracer in groundwater modeling.

Isotopic boron has been utilized to characterize the origin of nitrate sources including fertilizers, wastewater, and animal manure (Chetelat & Gaillardet 2005; Hasenmueller & Criss 2013; Widory et al. 2005). Palmer et al. (1987) found that, in groundwater and soil/clay interactions, boron can be affected by adsorption to clays. Goldberg (1997) reported that boron adsorption is highly dependent on solution pH. Boron present as uncharged boric acid (pH 4 to 8) is much less affected by clay adsorption than in the borate anion form that is present in solutions between pH 9 and 10. In groundwaters with nearly neutral pH values (pH 5-7), Barber et al. (1998) showed that boron has the same transport characteristics as chlorides, is unique to sewage sources, and seems unaffected by adsorption to soils.

In this paper, the karst, urbanized springshed for Volusia Blue Spring (VBS) located in east central Florida was chosen as the study site because the primary nutrient sources (i.e. septic systems, wastewater treatment facilities, and fertilized areas) are characteristic of sources containing boron. CFT models have been developed in karst aquifers by defining conduit networks (Xu et al. 2015). In the VBS springshed, conduit networks have not yet been identified. Although several groundwater models that include VBS exist but at a larger scale, they are without

contaminant transport or karst aquifer properties (AEI 2010; McGurk & Presley 2002; Sepúlveda et al. 2012). Three-dimensional CFT models of the VBS karst springshed are not available. Additionally, published boron CFT models in other regions of the country were also limited. From the literature, it appears that three boron transport models have been published, including two-dimensional models of a nuclear waste site in Nevada (Ahn 1997) and agricultural sites in California (Benson 1991; Tayfur et al. 2010).

A three-dimensional numerical CFT model coupling MODFLOW (Harbaugh et al. 2000) and MT3DMS (Zheng & Wang 1999) has been developed and used to quantitatively investigate the impacts of human activities on contaminant pollution to VBS. The purpose of this research study was to evolve current understanding of the role of contaminant loading on indicator levels within the VBS springshed. In this paper, we present the results of a three-dimensional numerical contaminant fate and transport model utilizing boron to simulate impacts on groundwater quality from multiple sources including septic systems, treated wastewater discharges, and fertilizers. In consideration of the urbanized development surrounding the impaired waters of the VBS, an investigation into the contaminant transport patterns is needed for making decisions regarding groundwater movement, spring protection, and restoration.

Volusia Blue Spring

The Volusia Blue Spring (VBS) is classified as a first magnitude spring, meaning that it discharges more than 100 ft^3/s (2.8 m^3/s) from the confining zone of the Upper Floridan Aquifer (UFA). The VBS is located along the section of the St. Johns River located near Orange City, Florida. The recharge area includes cities of Debary, Orange City, DeLand, Deltona, and unincorporated Lake County (Figure 9). Land surface elevations vary between 1.5 and 30 meters

above sea level with a datum of NGVD29. VBS is central to the model domain of this study. Prior evaluations of larger scale groundwater models produced delineations of the Blue Spring recharge area that comprised approximately 840 km^2 of mostly urbanized land use with an estimated population of 128,920 (AEI 2010; FDEP 2015).

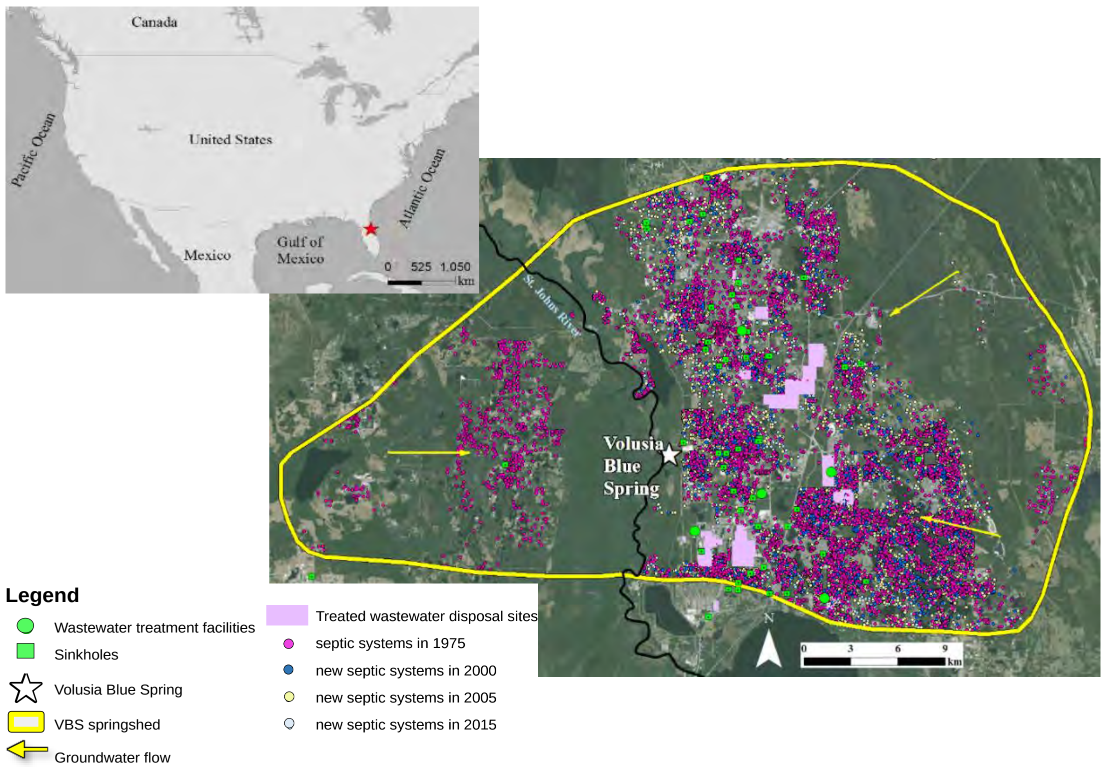

Figure 9: Location map of VBS and the pollutant sources within its recharge area

VBS is considered an Outstanding Florida Water (OFW) (Code, F.A. 2010) and was subject to regulations for a total maximum daily load (TMDL) for nutrients by the Florida Department of Environmental Protection (FDEP) in 2014 (Holland & Bridger 2014). Groundwater withdraws are regulated by the St. Johns River Water Management District (SJRWMD). Within the VBS recharge area, there are more than 230 active drinking water wells, more than 25,500 active septic systems, and five wastewater treatment facilities discharging more than 0.38 ML/d

of treated wastewater (FDOH, 2015; G. Robinson, SJRWMD, personal communication, 2015). While quantifiable impacts from wastewater sources within the Blue Spring recharge area have yet to be published, results from numerous water quality studies of other Florida spring basins imply that discharge from septic tank systems and treated wastewater discharge sites are major contributors (Katz, 1992; Katz & Hornsby, 1998; Oppenheimer, 2011; Phelps, 2004; Verstraeten et al., 2005).

Climate conditions

The climate in the Blue Spring region is humid subtropical with a rainy season occurring between the months of May and October. According to the NOAA weather stations in Lisbon and DeLand, the mean annual rainfall between the years 1975 and 2015 was 1344 mm/year and temperatures near Blue Spring varied from 20.9 to 22.9°C in 2014 (NOAA 2015). Evapotranspiration varies each year as a function of net radiation, temperature, wind speed, and humidity. According to the United States Geological Survey (USGS) Florida Evapotranspiration Network, the mean annual evapotranspiration rate in the springshed throughout the simulation period was 735 mm/year.

Hydrogeology

The groundwater system within the VBS recharge area consists of the unconfined surficial aquifer and the confined Floridan Aquifer System (FAS). As reported by Katz (1992), the thickness of the surficial aquifer is generally within the range of 6 to 15 meters, but can be as much as 30 meters in the high ridge areas of the DeLand Ridge. Discharge at the VBS is mostly from confined zones within the FAS. The top elevation of the FAS is near land surface at VBS. Beneath

the DeLand Ridge, the FAS occurs at depths of about 30 to 38 meters, and at depths of 23 meters in most other areas of the springshed (Vecchioli et al. 1990). The FAS is subdivided into the Upper Floridan Aquifer (UFL) and Lower Floridan Aquifer (LFA). According to Toth and Katz (2006), the surficial aquifer in proximity of the VBS is underlain by well-drained Holocene and Pleistocen sand, sandy silt and clay that form the intermediate confining unit. Highly transmissive limestone and dolomite from the Eocene and Paleocene Ages comprise the FAS. The UFA consists of limestone and dolomite from the Ocala/Suwannee and Avon Park Formation units, respectively (Toth & Katz 2006; SJRWMD 2011). The LFA consists of limestone and anhydrite from the Oldsmar and Cedar Keys Formation units, respectively (SJRWMD 2011).

There are three springs located within the model domain: Volusia Blue, Gemini, and Green. According to USGS observations in 2005, the mean discharge rate of Volusia Blue, Gemini, and Green springs were 3.8, 0.3, and 0.03 cm^3/s, respectively. In 2015, the mean discharge rate of Volusia Blue, Gemini, and Green springs were 3.8, 0.3, and 0.04 cm^3/s, respectively.

Characteristic of karst aquifers, particularly the VBS, is the sinkhole areas that provide rapid infiltration by direct connections between the surface and aquifer (Ravbar & Goldscheider 2009). The Florida Geological Survey (2015) reports that there are more than forty subsidence incidents, commonly known as sinkholes in the karst VBS recharge area.

Studies indicate that boron presence in the FAS below the St. Johns River may be the influence of relict seawater (Mercer et al. 1986; SJRWMD 2011; Weast et al. 1985). As evidenced by elevated chlorides thought to have been enabled by groundwater circulation patterns and soil adsorption, the SJRWMD (2011) reported the presence of relict seawater in the confining zones of the St. Johns River and VBS. Although discussion of boron was not included, the average boron content in seawater is 4.5 mg/L (Weast et al. 1985).

Methodology

A three-dimensional numerical contaminant fate and transport (CFT) model coupling MODFLOW (Harbaugh et al. 2000) and MT3DMS (Zheng & Wang 1999) was developed and employed to quantitatively investigate the impacts of anthropogenic boron loading to VBS. Here, the transport of boron as a conservative indicator assumes chemical reactions are negligible (Benson et al. 1991). Information on locations of conduits or fractures within the VBS recharge area was unavailable or simply does not exist. However, cells containing a sinkhole were assigned hydraulic conductivity and leakance values that were different from cells that do not have a sinkhole. Model inputs included boron data from septic tanks, treated wastewater disposal sites, fertilizer, and relict seawater. Model calibration was achieved through observations of groundwater level, spring discharge, and boron concentration in the surficial and Floridan aquifers.

The VBS recharge area was represented using a quasi-three-dimensional model comprising three layers: the surficial (layer 1), Upper Floridan (layer 2), and Lower Floridan aquifers (layer 3). The model domain consisted of 226,568 active grid cells, each equally spaced 76.2 meters in length and 76.2 meters in width. Input files from block-centered flow (BCF), well, river, drain, general head (GHB), recharge, and constant head (CHD) packages were processed utilizing Groundwater Vistas version 6 (GWV_6).

In the 41-year simulation period (1975-2015), drinking water wells, reclaimed water use and septic systems were characterized as individual wells at varying depths with varied flows between stress periods. Historical drinking water flow data was unavailable, however, the pumping rates were available for the year 2015. Therefore, it is assumed that the pumping rate increased at a rate of 50% over the 41-year simulation period. Recharge rates were obtained from larger scale

groundwater models that include the Volusia Blue Spring (AEI 2010; Sepúlveda 2012) but were calibrated and adjusted where needed. River stage boundary head and mean boron concentrations were based on interpolations of the mean water levels recorded by SJRWMD between the years 1975 and 2015 and limited boron concentration data within the springshed.

Input Parameters

In groundwater environments, Bassett (1998) had shown that boron is stable and unaffected by oxidation, reduction and/or biological reactions. Although Goldberg (1997) reports that in some groundwater and soil interactions, a fraction of the total boron may be adsorbed to the clays of the intermediate confining unit. However, due to the pH conditions of the VBS aquifer (pH 4-8) and the spatial frequency of sinkholes that connects the surficial aquifer to the confined aquifer (Ravbar & Goldscheider 2009), it has been reasonably assumed that most boron in the VBS springshed transports from the surficial aquifer to the confined aquifer with negligible transformation or adsorption.

Natural Recharge

Natural recharge is assumed as the difference between precipitation and the sum of evapotranspiration and runoff. Natural recharge varies by each stress period and is based on the average estimated recharge by water balance. The average boron content in two groundwater monitoring wells located in fertilized areas within the springshed was 50 μg/L. Therefore, urbanized recharge was supplied a boron concentration of 50 μg/L to represent land applied fertilizer.

Artificial Recharge

Artificial recharge is the reclaimed irrigation areas within the springshed. Actual reclaimed flow data was obtained from FDEP for wastewater treatment facilities, where discharge more than 0.1 million gallons per day (0.378 ML/day) was simulated throughout the stress periods. In this study, observations of boron were taken at each of the wastewater facilities in the springshed. The mean boron content observed from these wastewater treatment facilities and utilized in the model was 200 µg/L.

Reclaimed irrigation was modeled as one injection well to the surficial aquifer per grid cell that overlies a reclaimed water irrigation area. The calculation performed for each grid cell within a reclaimed water irrigation area is shown in Eqn (1) where Q_n is the flow rate per grid cell, Q_T is the actual flow rate of the total irrigation area, and N_T is the number of grid cells over the total irrigation area. Actual wastewater treatment discharge flow data (Q_T) and the number of grid cells (N_T) utilized to represent the discharge from each facility is summarized in Table 5, where **Table 5: Summary of actual flow data for wastewater treatment facilities within the VBS recharge area**flows were obtained from monthly operating reports for each facility.

$$Q_n = \frac{Q_T}{N_T} \quad (1)$$

Table 5: Summary of actual flow data for wastewater treatment facilities within the VBS recharge area

Wastewater Treatment Facility ID	1996 Flow (ML/day)	2005 Flow (ML/day)	2015 Flow (ML/day)	Number of Grid Cells
1	2.0	3.2	5.3	692
2	0.97	1.1	1.7	205
3	0.95	0.69	1.0	6
4	3.9	4.3	5.5	173
5	2.1	3.2	3.1	867

Initial Concentration

Initial concentrations were appointed to the Upper and Lower Floridan aquifers. Based on observed boron concentrations within the Floridan aquifer of the springshed, a background concentration of 17 μg/L was utilized for this model. SJRWMD (2011) reports that relict seawater exists beneath the St. Johns River, and while boron data in the Floridan aquifer beneath the St. Johns River near VBS was unavailable, seawater has been reported to contain an average of 4,500 μg/L of boron (Weast et al. 1985). The elevated presence of relict boron within layers 2 and 3 was estimated and calibrated from the extent of relict chlorides (SJRWMD 2011).

Water Use Wells

Water use location, depth, and flow data within the year 2015 was utilized for estimated pumping rates within the springshed (G. Robinson, SJRWMD, personal communication, 2015). Since historic water use data was unavailable, it is assumed in the model that from the year 1975 to 2015, pumping increased by 50% based on the population growth.

Septic Systems

Data collected from the Florida Department of Health's septic tank inventory (FDOH, 2015) was utilized to spatially and historically simulate each of the 25,539 septic systems within the VBS recharge area. As shown in Table 6, the groundwater model simulates five stress periods in which individual septic systems were introduced to the recharge area as injection wells to the surficial aquifer in the Well Package. The boron concentration in modeled septic systems was

determined from observations in septic tanks located throughout the springshed. The concentration of boron discharging from septic systems was appointed a value of 80 μg/L, as determined from the average boron content observed in nine residential septic tanks within the VBS springshed. The discharge rate from each septic system was provided a value of 708 L/day (Hazen & Sawyer 2009). The total number of septic systems represented within each stress period is summarized in Table 6.

Table 6: Number of individual septic systems in each stress period of the VBS model

Stress Period	Stress Period Type	Time Period	Total number of septic systems
1	Steady-state	1975-1990	6,200
2	Transient	1990-2000	8,658
3	Transient	2000-2005	18,593
4	Transient	2005-2015	25,539
5	Transient	2015-2016	25,539

Rivers

River boundary conditions were assigned to features that can remove and/or infiltrate water across the surficial and Upper Floridan aquifers. River stage boundary head and mean boron concentration (60 μg/L) was based on interpolations of the mean water levels recorded by the SJRWMD between the years 1975 and 2015 and limited boron concentration data within the springshed. Conductance values from nearby areas (AEI 2010) were calibrated to achieve reasonable head and concentration values.

Drains

Three springs were simulated as drains that remove water in the UFA of the VBS model domain. Obtained conductance values (AEI 2010) were calibrated to achieve spring discharge values that are close to observed values. The stage of each drain is based upon the mean stage recorded by the USGS between the years 1975 and 2015.

General Head

General head boundary conditions surrounded the model domain in the layers. The boron concentration of the general head boundaries in the surficial and Floridan aquifer was equivalent to surrounding initial concentration values. Since sufficient water level observations wells surrounding the model domain were unavailable, surficial aquifer head conditions were interpolated from 2005 contour data (AEI 2010). Upper and Lower Floridan aquifer head conditions were interpolated from September, 2005 USGS potentiometric maps. Conductance values from nearby areas (AEI 2010) were calibrated to achieve reasonable head and concentration values.

Transport Parameters

Transport parameters remain constant throughout the model simulation and are listed in Table 7.

Table 7: Transport parameters for VBS model (Hickey 1989; Hutchings & Tarbox 2003; Mercer et al. 1986)

Parameter	Value
Porosity	0.4 surficial; 0.2 Floridan
Horizontal longitudinal dispersivity	3 m
Horizontal transverse dispersivity	0.01 m
Vertical transverse dispersivity	0.01 m

Results

Calibration and Validation

Calibration was performed for the year 2005 with validation performed for the year 2015. Because of limited data availability, there are less calibration than validation targets. For the year 2005, a total of six head and three flux calibration targets were used in the UFA and nine head targets in the surficial aquifer. For the year 2015, a total of ten head, three flux, and twelve concentration targets were used in the UFA and twelve head and five concentration targets were used in the surficial aquifer. The targets used in the year 2015 are shown in Figure 10 and the resulting RMSE of each target in the years 2005 and 2015 is provided in Table 4.

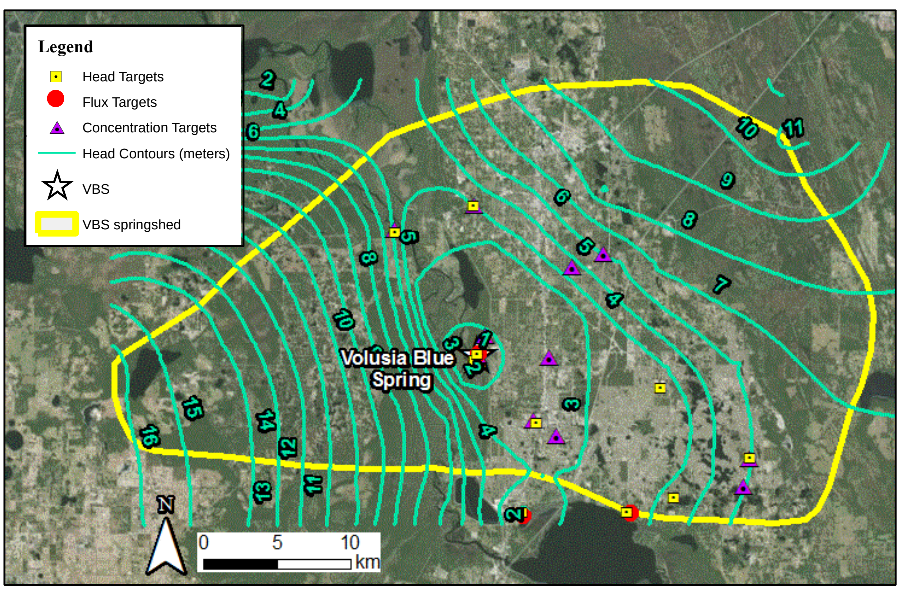

Figure 10: Target distribution and model results of 2015 simulated head contours in the UFA, datum NGVD 29

Table 8: Summary of RMSE for head, concentration, and flux targets

Target type	Unit	2005 RMSE	2015 RMSE
Head	meters	1.8	1.8
Concentration	µg/L	17.7	17.7
Flux	m^3/sec	0.11	0.12

The calibrated model is reasonable with calculated estimates of actual recharge. The average estimated recharge balance is approximately 344 mm/year whereas the average modeled recharge (natural and artificial) is approximately 390 mm/year. Target heads were based upon mean groundwater levels observed in monitoring wells maintained by SJRWMD. Recharge and leakance coefficients were calibrated and adjusted using a trial-and-error approach to minimize the difference between observed and computed heads in the surficial and Upper Floridan aquifers. Heads and flux heads at drain locations were based upon mean stage levels recorded by SJRWMD and USGS at springs located within the study area. Drain conductance was calibrated and adjusted using a trial-and-error approach to minimize the difference between observed and computed discharges at each spring (drain).

Given that VBS discharge is mostly from the Floridan aquifer, computed boron values were calibrated against observed boron values in the UFA throughout the springshed. Concentration targets rely on mean boron concentrations observed at the spring's vent and in drinking water and monitoring wells spatially located in the UFA throughout the springshed. The initial concentration values within the Floridan aquifer were calibrated and adjusted using a trial-and-error approach to minimize the difference between observed and modeled boron concentrations in the UFA.

Boron transport in the UFA is shown in Figure 11. The limits of increased boron concentrations in the UFA are similar to the limits of the elevated chlorides present beneath the St.

Johns River that have been determined to originate from relict seawater influences (SJRWMD 2011).

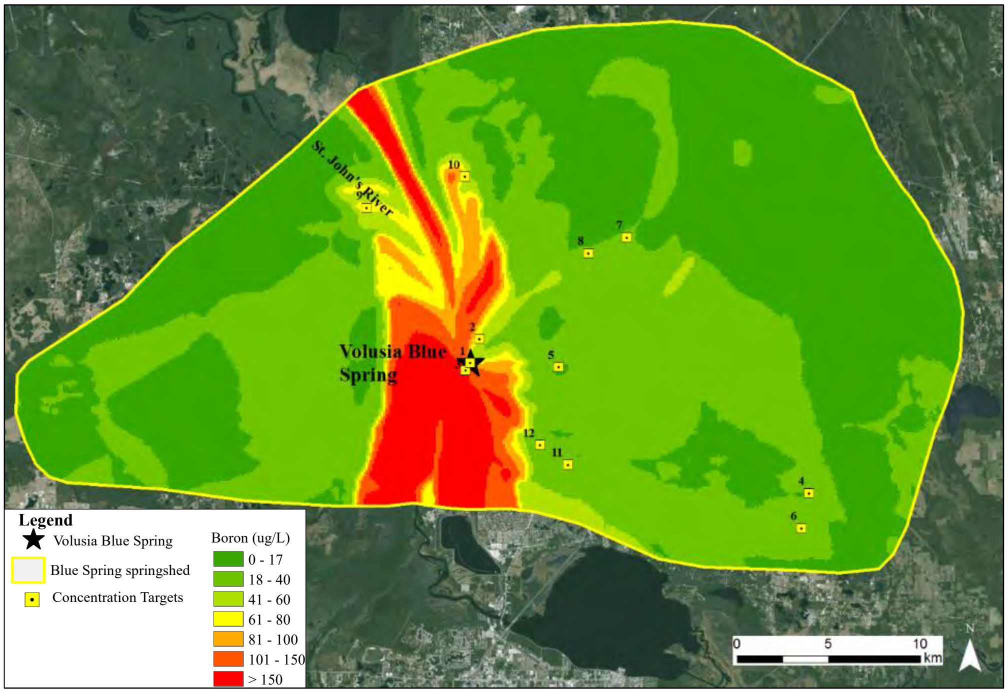

Figure 11: Simulation results of boron transport through UFA in 2015

Sensitivity Analysis

A sensitivity analysis was performed on calibrated model parameters and boundary conditions to determine the effect on calibration statistics. The sensitivity analysis was performed on recharge, hydraulic conductivity, and general head values using four multiplying factors. A plot of the RMSE versus the multiplier for each variable is shown in Figure 12. From these results, it is determined that head is the most sensitive to changes in river stage and that concentration is the most sensitive to changes in hydraulic conductivity.

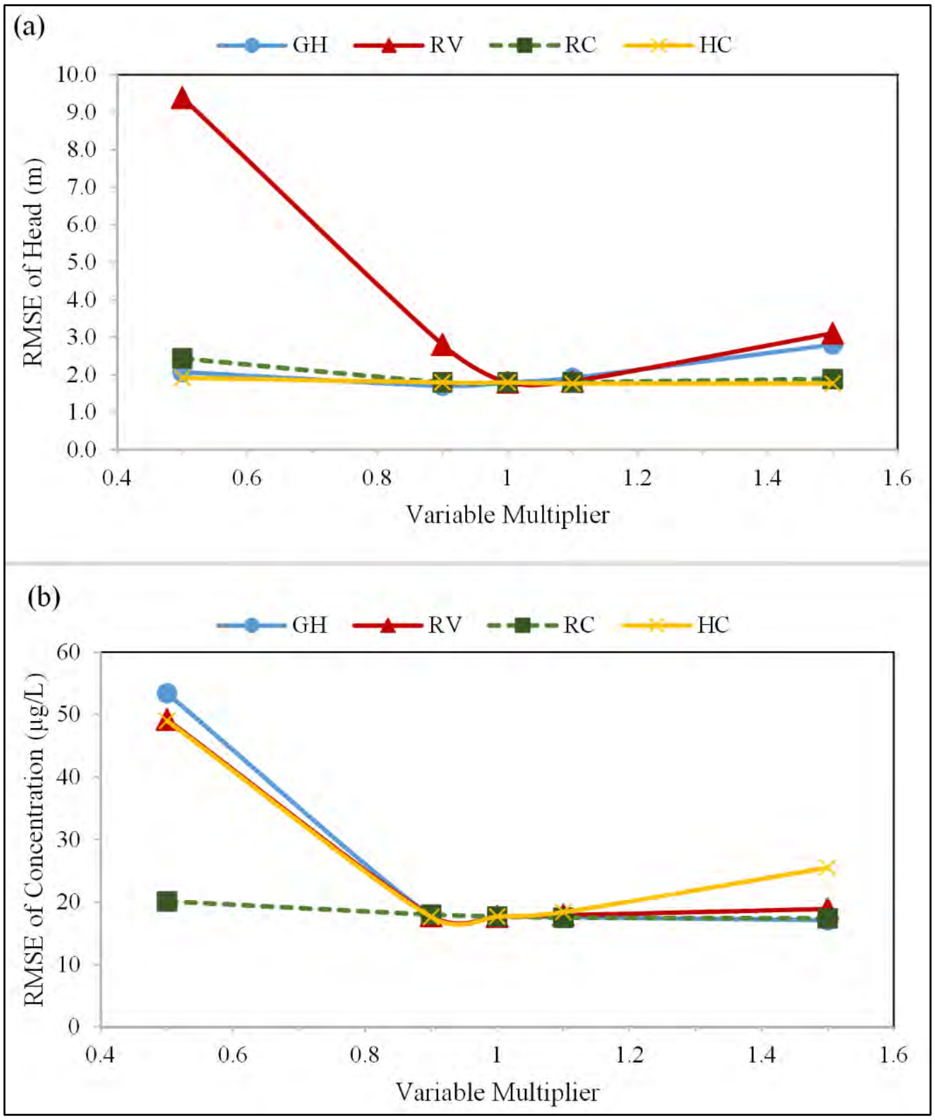

Figure 12: Results of sensitivity analysis for (a) head, and (b) concentration

Extent of Contaminant Transport

Boron concentrations were utilized as indicators of both anthropogenic activity and relict seawater. The overall spatial distribution of boron in the UFA is shown in Figure 11. Excluding relict seawater influence, the boron transport from anthropogenic activity in the UFA is shown in Figure 13. From simulated results of 2015 conditions, the boron concentration at the spring

discharge with and without relict sweater influence was 130 and 20 µg/L, respectively. Numerical simulations in the year 2015 show that boron from treated wastewater discharge sites has not reached spring discharge (Figure 13d).

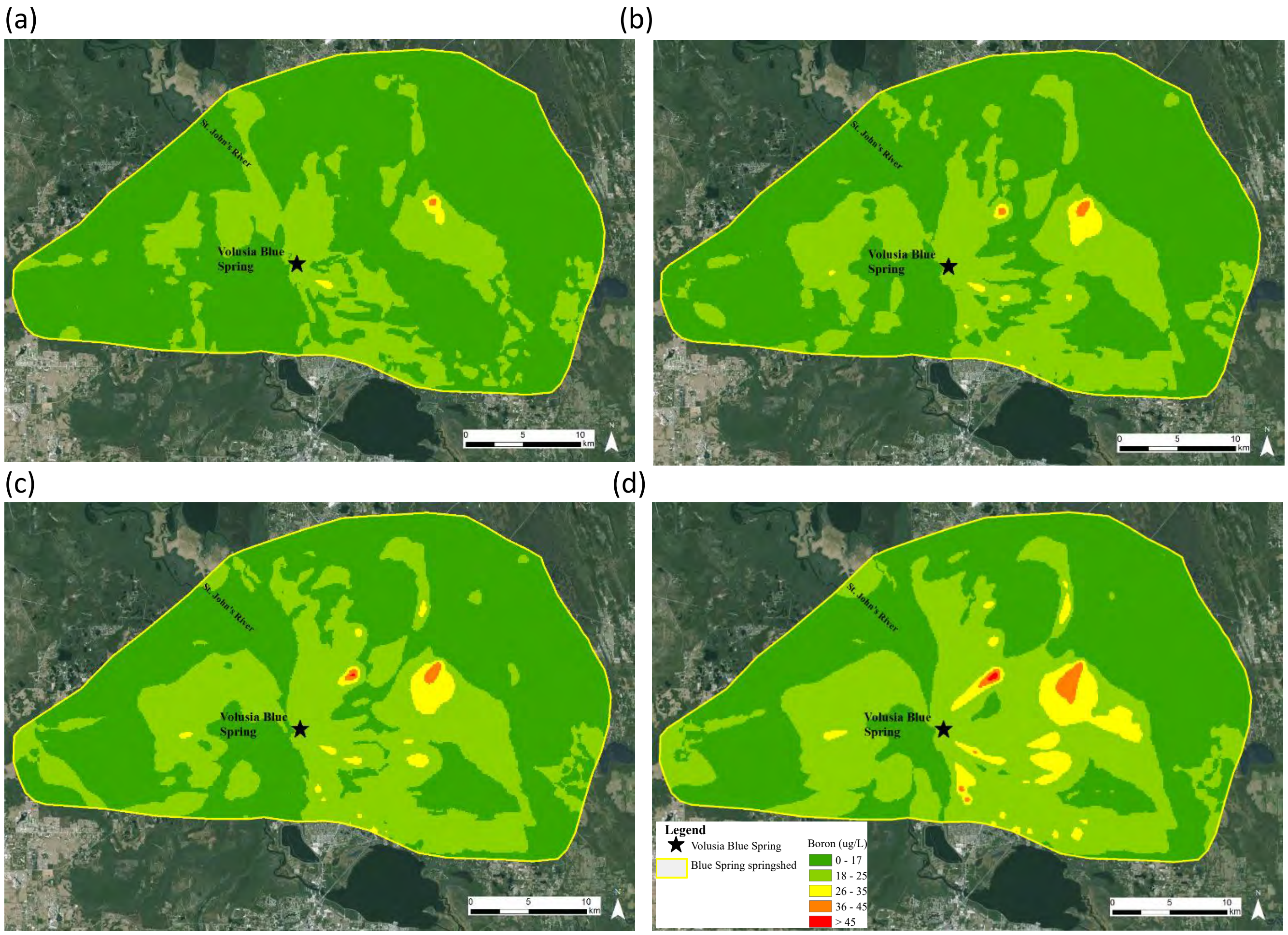

Figure 13: Simulation results in the UFA showing an increase of boron in both space and time from septic systems, wastewater treatment facilities, and fertilizers, excluding relict seawater influence, for (a) 1990, (b) 2000, (c) 2005, and (d) 2015

Discussion

Model results define 822 km^2 of recharge area contributing to the discharge at VBS. Results indicate that water from the surficial aquifer in surrounding urban areas to the east, northeast, and

southeast significantly contributes to the water quality at the VBS vent. As demonstrated by the transport of treated wastewater discharge, the model appears to be reasonably accurate at predicting the transport of conservative indicators such as boron. A permit search within FDEP's wastewater treatment facility database found that the first domestic wastewater treatment facility in the springshed began operation approximately thirty years ago. Through water quality analyses, Toth and Katz (2006) estimate that spring water at VBS is more than thirty years of age. The VBS model supports this spring age estimate in that it demonstrates the boron contained in treated wastewater effluent has not yet reached VBS (Figure 13d). From Figure 13, the greatest concentrations of boron apply to specific areas, primarily near septic tanks and treated wastewater discharges, not the entire urbanized region as significant impacts from fertilizers may suggest. From Figure 13a, higher boron concentrations occur in two areas where treated wastewater discharge did not yet exist, indicating septic system impact in these two areas. Advancement through space and time (Figure 13b-c) indicates both septic systems and treated wastewater discharge sites influence increased boron concentrations approaching VBS in the UFA.

A limitation of the developed model is the assumption that groundwater flows through porous media rather than through a fractured conduit system that is characteristic of karst aquifers (Shoemaker 2004). Due to the complexity of karst aquifers and limited availability of conduit and fracture data in the springshed, the VBS model relied on porous media properties simulated through modifications to hydraulic conductivity and leakance values within sinkhole locations. Results of utilizing MODFLOW-2000 and MT3D to simulate contaminant transport within the karst springshed surrounding VBS yielded head and concentration RMSE values of 1.8 meters and 17.7 μg/L, respectively.

In the VBS model, anthropogenic nutrient sources were simulated as either recharge water or individual wells supplied with unique concentrations based upon observed data. The distinctive qualities of each anthropogenic nutrient source contained in the VBS model offer the ability to predict the effects of groundwater and spring protection and restoration strategies, particularly those related to reduced nutrient loadings (Holland & Bridger 2014), on groundwater and spring discharge. The assumptions made herein are adequate for the general purposes of this research, but when simulating projections, flow and concentrations do not transport as darcian and multi-nodal transport is not accounted for. The general nature of the developed model lends itself to be utilized as a predictive tool in support of future pollution prevention planning in the VBS springshed.

Conclusions

The objective of this study was to produce a three-dimensional numerical CFT model capable of simulating the impact of a conservative tracer to groundwater flow at VBS from urbanized practices. Using boron as a tracer from sources including treated wastewater, septic systems, and fertilizers, the model relied on recharge, initial concentrations, porosity, and dispersivity parameters to simulate boron transport. Karst properties were represented at sinkhole locations by use of calibrated hydraulic conductivity and leakance values. The developed model was calibrated with boron observations collected from twelve groundwater wells, fifteen septic tanks, and five wastewater treatment facilities within the VBS springshed. This work is novel in that 1) it is the first three-dimensional boron transport model of a karst aquifer in Florida; and 2) it is the first CFT model of a central Florida spring.

The numerical simulations indicate that most of the boron observed at the VBS vent originates from relict seawater migration (Figure 11). However, anthropogenic boron is observed in the 2015 simulation (Figure 13). From 2015 simulated results, it appears that septic systems and wastewater treatment facilities just east and southeast of the VBS vent are the primary sources of current anthropogenic boron within the VBS springshed. Given the limited information on fractures within the karst VBS springshed, additional experiments such as dye tests or lineament analyses are recommended for improved fracture identification. Utilizing existing CFT models, further research is needed to simulate contaminant reduction in the environment to efficiently promote pollution prevention planning.

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CHAPTER FIVE: PREDICTING AND EVALUATING NITRATE MANGAEMENT SCENARIOS IN THE VOLUSIA BLUE SPRING SPRINGSHED

Abstract

In the Volusia Blue Spring (VBS) recharge area of Florida (United States), decades of anthropogenic loadings have impacted the quality of spring water discharged from the confined aquifer. For the first time, MODFLOW-2000, MT3DMS, and field data were employed to develop a calibrated three-dimensional numerical contaminant fate and transport model for use as a nitrate management planning tool for VBS. The model relied on population growth projections and nitrogen data from treated wastewater discharge, septic tanks, and fertilized areas. The calibrated VBS nitrate model yielded a root-mean-square-error of 0.17 mg/L throughout the springshed and a 13.6% difference between observed and modeled nitrate concentration at spring discharge. Simulation results from four nitrate management scenarios were used to estimate a preliminary conceptual opinion of probable construction cost that is compared to mg/L of nitrate mitigated. It was determined that constructed wetlands and targeted septic system removal are the two most cost effective nitrate management scenarios. However, septic system removal results in the greatest benefit with a 36% nitrate decrease in a forty-year projection of discharge water quality.

Keywords

septic tank, anthropogenic, pollution prevention, MODFLOW, MT3D

Introduction

Historic anthropogenic practices have been shown to contribute boron, nitrate, metals, and bacteria to groundwater and spring discharge in karst aquifers (Reed, Wang, Duranceau 2015; Pronk et al. 2008; Vesper & White 2003; Xu et al. 2015). In the Volusia Blue Spring (VBS) recharge area, wastewater discharge practices are of rising concern since increased levels of nitrate have been recently observed at the spring vent (Holland & Bridger 2014; Reed, Wang, Duranceau 2015). The VBS has been recognized as an Outstanding Florida Water because its average nitrate concentration of 0.7 mg/L exceeds allowable levels proposed by the Florida Department of Environmental Protection (Holland & Bridger 2014). Nitrate is of particular concern in aquatic environments, as its elevated presence is known to stimulate algal growth (Stevenson et al. 2007) and affect diversity and productivity of flora and fauna in spring runs (Holland & Bridger 2014).

Utilizing field obtained data, a contaminant fate and transport (CFT) model of the karst VBS recharge area has been developed to show the non-reactive transport phenomena of anthropogenic boron (Reed, Wang, Duranceau 2015). The use of boron as an anthropogenic tracer showed that the spring's vent is currently impacted, in varying extents, by surrounding urbanization. Although boron has been shown as a co-migrant to nitrate in groundwater systems (Leenhouts et al. 1998), CFT models of anthropogenic boron are not capable of predicting the transport of reactive tracers, such as nitrate, due to exchange, adsorption, and biological uptake.

Wastewater discharges nitrogen into the environment initially as either total Kjeldahl nitrogen (TKN) from septic tanks or nitrate from treated wastewater. Nitrate is formed from the nitrification of unbound nitrogen in the presence of oxygen. In groundwater systems, nitrification occurs in the surficial aquifer at an estimated first-order rate constant of 0.008 day^{-1} (Zhu et al.

2015). Subsequent to nitrification and in the absence of oxygen, denitrification occurs. Nitrogen removal by exchange and biological uptake during transport in the groundwater system varies with estimates ranging from 25% to 80% (Anderson 2006; Zhu et al. 2015). Postma and Boesen (1991) determined that denitrification is the prevailing chemical reaction that alters nitrate in groundwater systems.

Nitrate CFT models have been developed to evaluate the impact of anthropogenic practices, including farming and septic tanks, in areas throughout northern Florida (Kincaid, Meyer, Day 2013; Zhu et al. 2015). CFT models simulating nitrate management scenarios (NMS) have been published but are limited and, CFT models simulating NMS impacts on a karst aquifer were not available. Although it appears that five CFT models with NMS have been published, they are confined to primarily agricultural basins in South Korea, France, and the United States – Colorado, Iowa, and Washington (Bailey, Gates & Romero 2015; Chaplot et al. 2004; Conan et al. 2003; Almasri & Kaluarachchi 2007; Lee et al. 2010).

A calibrated three-dimensional numerical CFT model (Reed, Duranceau, Wang 2015) coupling MODFLOW (Harbaugh et al. 2000) and MT3DMS (Zheng & Wang 1999) has been utilized to quantitatively investigate the impacts of NMS on nitrate levels within the groundwater and discharge of VBS. In this paper, we present the results of NMS simulations including retrofit to advanced septic systems, septic system removal, and the installation of constructed wetlands. In consideration of the urbanized development surrounding the impaired waters of the VBS, pollution prevention planning is needed for making decisions on groundwater and spring protection.

Materials and Methods

The VBS recharge area was chosen as the study site because it is refuge to hundreds of manatees in winter months and is surrounded by anthropogenic nitrate sources including more than 25,500 active septic systems and five wastewater treatment facilities (FDOH 2015). The VBS is located in central Florida, along the St. Johns River, and comprises approximately 822 km^2 (Figure 14).

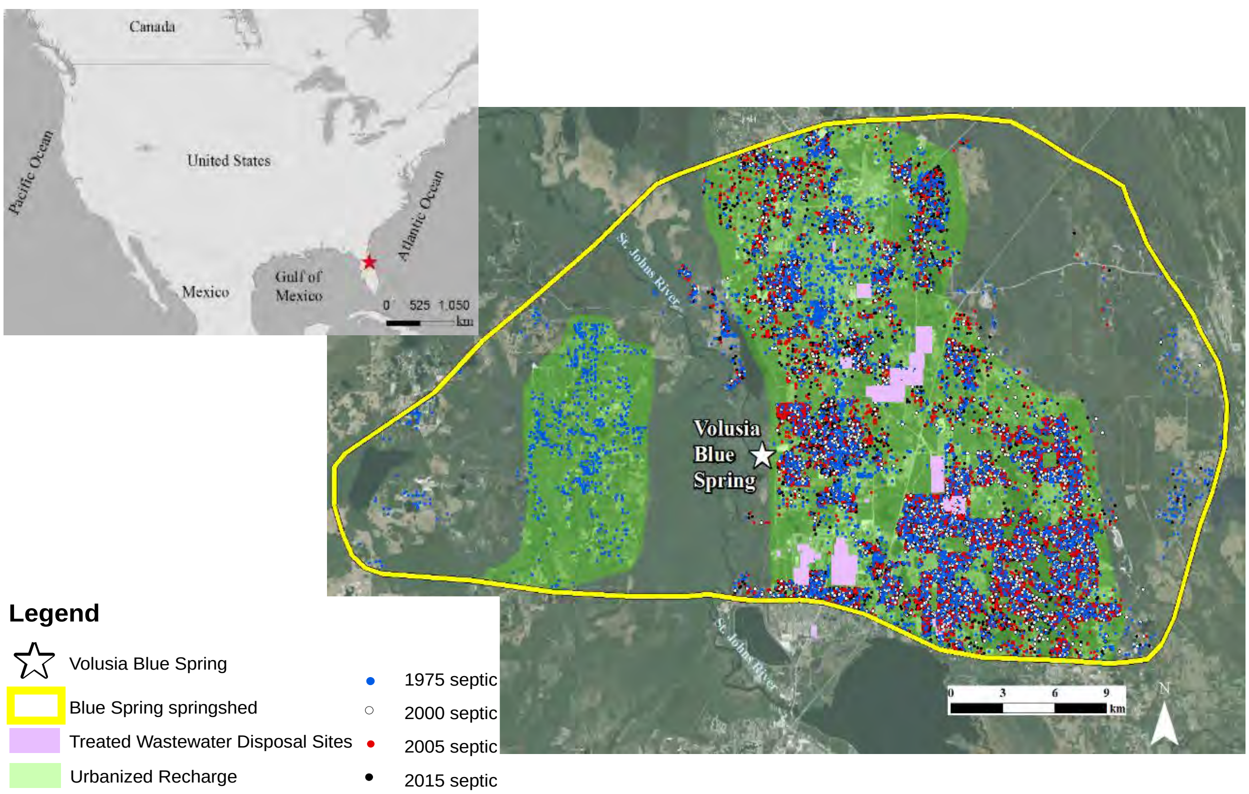


Figure 14: Location map of VBS and anthropogenic nitrate sources within its recharge area

Utilizing MODFLOW (Harbaugh et al. 2000) and MT3DMS (Zheng & Wang 1999), a three-dimensional numerical CFT model (Reed, Wang, Duranceau 2015) was employed to

quantitatively evaluate future impacts of anthropogenic nitrate loading to VBS. Here, the transport of nitrate from anthropogenic sources is simulated through the process of denitrification in the upper and lower Floridan aquifers (Conan et al. 2003; Reddy 1980; Zhu et al. 2015). Steady-state simulations with varying contaminant sources by year were conducted for a 41-year period (1975-2015) and a forty-year projection period (2015-2055). Model inputs included anthropogenic nitrogen data from septic tanks, treated wastewater disposal sites, and fertilized areas within the springshed. Input files from block-centered flow (BCF), well, river, drain, general head (GHB), recharge, and constant head/concentration (CHD) packages were processed utilizing Groundwater Vistas version 6 (GWV_6). Model calibration and validation was achieved through historical and current observations of nitrate concentrations in the surficial and Floridan aquifers.

Governing Equation

The governing equation for the contaminant transport is described in the following partial differential equation (Zheng and Wang 1999):

$$\frac{\partial(\theta C^k)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D \frac{\partial C^k}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(\theta v C^k) + q_s C_s^k + \sum R_n \qquad (2)$$

where

θ is the porosity [--];

C^k is concentration of species k [ML^{-3}];

t is time [T];

x_{ij} is the distance along the respective Cartesian coordinate axis [L];

D is the hydrodynamic dispersion coefficient tensor [L^2T^{-1}]

v is the pore water velocity [LT^{-1}];

q_s is the sink/source of fluid per unit volume [T^{-1}];

C_s^k is the concentration of source/sink for species k [ML^{-3}];

$\sum R_n$ is the chemical reaction term as a function of ρ_b [$ML^{-3}T^{-1}$]

ρ_b is bulk density (ML^{-1}].

Boundary conditions and aquifer properties

Flow

Recharge, water features, and wastewater discharges were utilized as flow inputs into the model (Reed, Wang, Duranceau 2015). Water use wells and treated wastewater discharge flows were adjusted in correspondence to an increased annual population growth projection of 1.5% (Quentin L. Hampton Associates, Inc., City of DeLand Wastewater & Reclaimed Water Master Plan Update, unpublished report) beginning in year 2015 and continuing throughout the simulation period (Table 9). Septic systems were also supplied with population projection increases, however, in the year 2035 septic systems were assumed to be "built-out" with subsequent flows remaining constant.

Table 9: Wastewater discharge in each stress period of the VBS-NMS model

Stress Period	Time Period	Septic system discharge (ML/d)	Treated wastewater discharge (ML/d)
1	2015-2016	18.1	16.7
2	2016-2025	21.0	19.4
3	2025-2035	24.4	22.5
4	2035-2045	24.4	26.1
5	2045-2055	24.4	30.3

Anthropogenic nitrate sources

Fertilizers, treated wastewater discharges, and septic systems were utilized as nitrate inputs into the model (Table 10).

Table 10: Input properties for VBS-NMS model

Input Property	Nitrate content (mg/L)
urbanized recharge[1]	0.5
septic systems[2]	70
treated wastewater discharge[3]	12

[1]The average nitrate content in samples collected from a retention pond and groundwater monitoring well, each located in fertilized areas within the springshed, was 0.5 mg/L. Therefore, approximately 550 km^2 of urbanized recharge was supplied a nitrate concentration of 0.5 mg/L to represent land applied fertilizer. [2]Septic systems were appointed a nitrate discharge value of 70 mg/L, as observed from TKN concentrations of septic tank supernatant taken from ten residential septic tanks within the VBS springshed. This nitrate concentration for septic tanks is based on the assumption that most of the TKN converts to NO_3 in the presence of oxygen (Katz 2010). [3]Nitrate concentrations of modeled treated wastewater discharge corresponds to the maximum discharge concentration permitted (FDEP 2015).

Nitrogen reactions

In groundwater systems, the dominant reaction in the alteration of nitrate is denitrification (Postma & Boesen 1991), which occurs in the confined zones without the presence of oxygen. For the study area, denitrification is considered the only reaction that alters the nitrate concentration in the groundwater. Denitrification is simulated as a zero-order reaction (Reddy 1980) with no sorption (Almasri & Kaluarachchi 2007). A value of 1.42 g/m^3 was used for bulk density (Zhu et al. 2015) and a value of 11 days was used for the half-life (Conan et al. 2003).

Nitrogen Management Scenarios (NMS)

Wastewater discharges have been shown to currently affect the water quality at VBS (Reed, Wang, Duranceau 2015). NMS applied to VBS included the fate and transport of nitrate through forty-year projections of baseline ("do-nothing"), sewered septic system areas, advanced septic systems, and constructed wetlands. With the exception of baseline, Figure 15 shows each NMS evaluated as part of this study.

Baseline ("do-nothing")

The baseline scenario predicts future anthropogenic nitrate loading to groundwater and spring discharge as a result of continuing current land use practices throughout the simulation period. Anthropogenic nitrate sources include septic systems, treated wastewater, and urbanized recharge.

Sewered septic system areas

In this scenario, beginning in year 2016, flow from septic systems was routed to the nearest treated wastewater disposal area. Treated wastewater has a greater nitrogen removal efficiency than septic systems, therefore, the total volume of untreated wastewater discharged to the recharge area was decreased. As depicted in Table 11, the total flow to treated wastewater disposal sites was increased by the flow in septic systems removed, however, the nitrate concentration in the treated wastewater effluent remained unchanged. Two septic system scenarios were simulated, select-sewered, where 7,497 septic systems were removed (Figure 15a), and all-sewered, where each of the septic systems were removed (Figure 15b).

Table 11: Summary table of treated wastewater flows in springshed, pre- and post- sewered improvements

Sewered areas	Number of septic systems removed	No. of treated wastewater disposal cells	Pre-sewer treated wastewater flow (ML/day)	Post-sewer treated wastewater flow (ML/day)
select (Figure 15a)	7,497	2,385	15.6	20.9
all (Figure 15b)	25,539	2,385	15.6	33.7

Advanced septic systems

Currently, in the VBS springshed, more than 97% of the septic systems are conventional systems in which very little nitrogen removal occurs (Roeder & Ursin 2013). Advanced septic systems employ air to provide, on average, 30% nitrogen removal in septic system discharge to the environment (Roeder & Ursin 2013). In this scenario, beginning in year 2016, each septic system was converted to an advanced system in which 30% less nitrogen was discharged to the environment (Figure 15c).

Constructed Wetlands

In the mid-1980's, 1,200 acres of constructed wetlands permitted to treat 132.5 ML/d were added for nutrient removal of treated wastewater discharge (FDEP 2011). Similarly, in this scenario, four areas within the springshed were supplied constructed wetlands to treat a total of 56.8 ML/d (Figure 15d). This set of constructed wetlands is intended to treat nitrate-rich groundwater from the surficial aquifer. Constructed wetlands were simulated as four pairs of boundary condition wells, each consisting of a 14.2 ML/d withdrawl well and a 14.2 ML/d

downstream discharge well. The nitrate concentration in the discharge water was appointed a value of 0.1 mg/L.

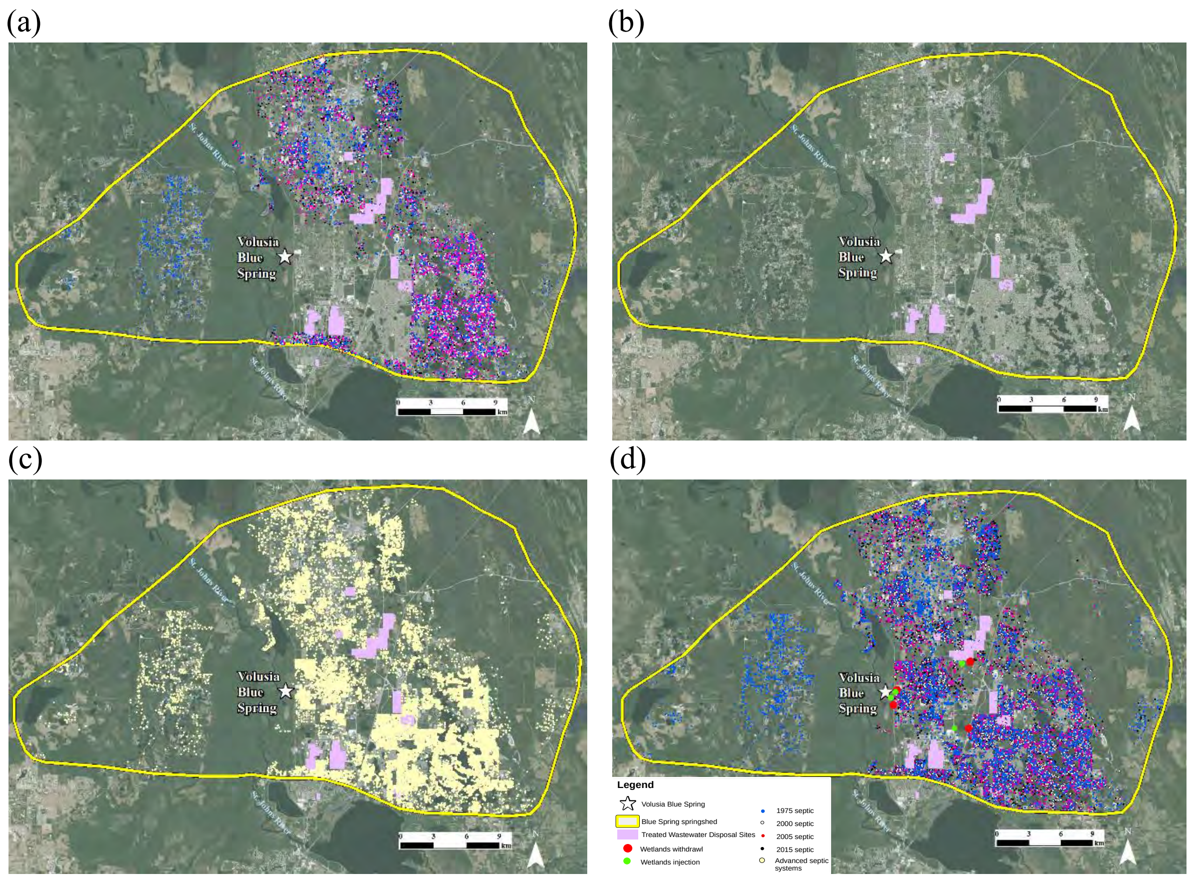


Figure 15: Nitrate management scenarios for (a) select-sewered, (b) all-sewered, (c) advanced septic systems, and (d) constructed wetlands

Results

Calibration and validation

Calibration was performed on the 2005 baseline model and was based upon the availability of historic nitrate measurements in existing monitoring wells throughout the surficial and confined aquifers of the springshed. Mean nitrate observations from a total of four monitoring wells

(Webapub 2015) were used as nitrate calibration targets in the model (Figure 15d). Although considerable effort has been made in the determination of nitrogen transport in the environment (Cabrera 1993; Conan et al. 2003; Katz et al. 2010; Postma & Boesen 1991), in water and soil environments, the chemistry of nitrogen is complex because of the occurrence of geochemical reactions such as denitrification, plant uptake, and/or soil retention that alter its oxidation state. Therefore, the reaction rate constant and nitrate concentrations in initial conditions, rivers, and lakes were calibrated and adjusted using a trial-and-error approach to minimize the difference between observed and simulated nitrate concentrations in the year 2005. Calibration results indicate a root-mean-square-error (RMSE) of 0.17 mg/L between observed and modeled nitrate throughout the springshed. After calibration, the denitrification reaction rate constant is 10^{-7} day^{-1}; initial nitrate concentration in the surficial and confined aquifers is 0.10 and 0.05 mg/L, respectively; and the nitrate concentration in rivers and lakes is 0.2 mg/L.

After calibration, validation was performed on the 2015 baseline model. A validation target was placed at the VBS vent. The data at this validation target is based on the average nitrate concentration of ten samples taken directly from the VBS vent, as part of this study, between the months of April and August, 2015. The average nitrate concentration of these samples was 0.7 mg/L. Nitrate data from seven other monitoring wells (Webapub 2015) was also compiled for use as nitrate validation targets in the model (Figure 15d). In the year 2015, results show a RMSE of 0.20 mg/L between observed and modeled nitrate throughout the springshed and an error of 13.6% between observed and modeled nitrate at the spring discharge. The acceptable calibration and validation results affirm that the baseline model is applicable for scenario-based projections.

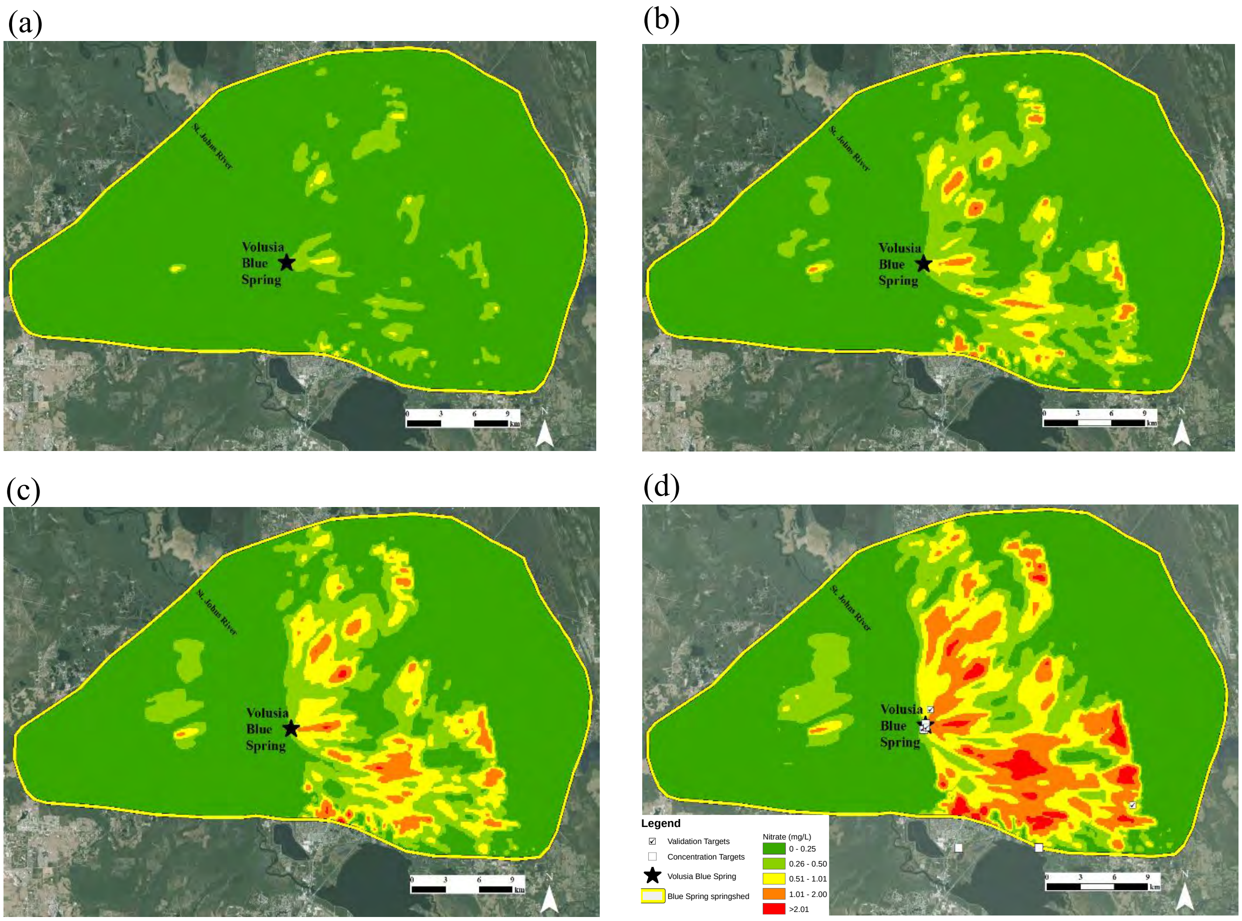


Figure 16: Simulation results in the UFA showing an increase of nitrate in both space and time from septic systems, wastewater treatment facilities, and fertilizers for (a) 1990, (b) 2000, (c) 2005, and (d) 2015 with calibration and validation targets

Extent of Contaminant Transport

The transport of anthropogenic nitrate in the UFA is shown in Figure 16. Actual nitrate data at the VBS vent from the year 1990 was not available, but from simulation results, the nitrate concentration at VBS increased from 0.18 mg/L in the year 1990 to 0.7 mg/L by the year 2015. Numerical simulations in the year 2015 show that nitrate from a portion of the treated wastewater discharge sites has reached spring discharge (Figure 16d).

NMS Projections

Forty-year projections of NMS from wastewater sources on VBS were simulated to evaluate the effect on nitrate concentrations in the VBS discharge. Figures 17a through 17e show the spatial distribution of nitrate in the UFA in the year 2055. From the simulated results of baseline conditions, it is estimated that VBS discharge will contain 1.8 mg/L nitrate in the year 2055 (Figure 17f). However, if septic systems are removed, nitrate is estimated to be 36% less than baseline predictions. The addition of constructed wetlands or the conversion to advanced septic systems show that future nitrate concentrations are 25% and 17% less than baseline, respectively.

Because the select-sewered scenario involved septic system removal in close proximity to VBS (Figure 15a), similar effects were demonstrated between the select-sewered and the all-sewered scenarios in the forty-year projection period (Figures 17b & 17c). Nitrate from septic systems in the all-sewered scenario does not reach VBS by year 2055. It is estimated that, by the year 2115, the all-sewered scenario will result in 17% less nitrate in spring discharge than the select-sewered scenario.

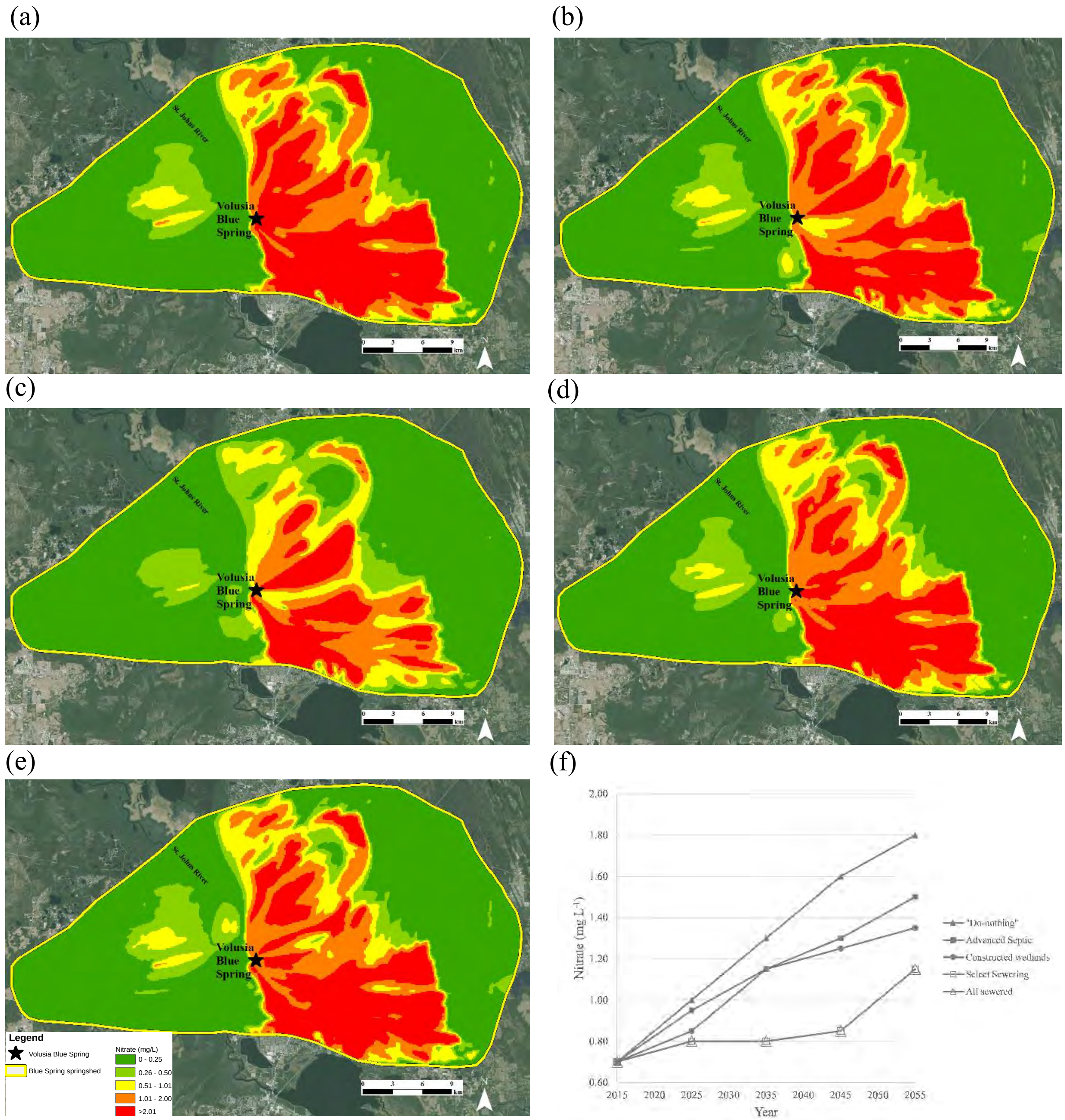


Figure 17: Simulation predictions for the year 2055 in the UFA showing nitrate transport in both space and time from NMS including (a) baseline, (b) select-sewered areas, (c) all-sewered areas, (e) advanced septic systems, (e) constructed wetlands, and (f) projected nitrate concentrations at VBS. Nitrate declines from "do-nothing" in the scenarios tested, but declines the most when septic systems are removed.

Preliminary Conceptual Opinion of Probable Construction Cost for Scenario Implementation

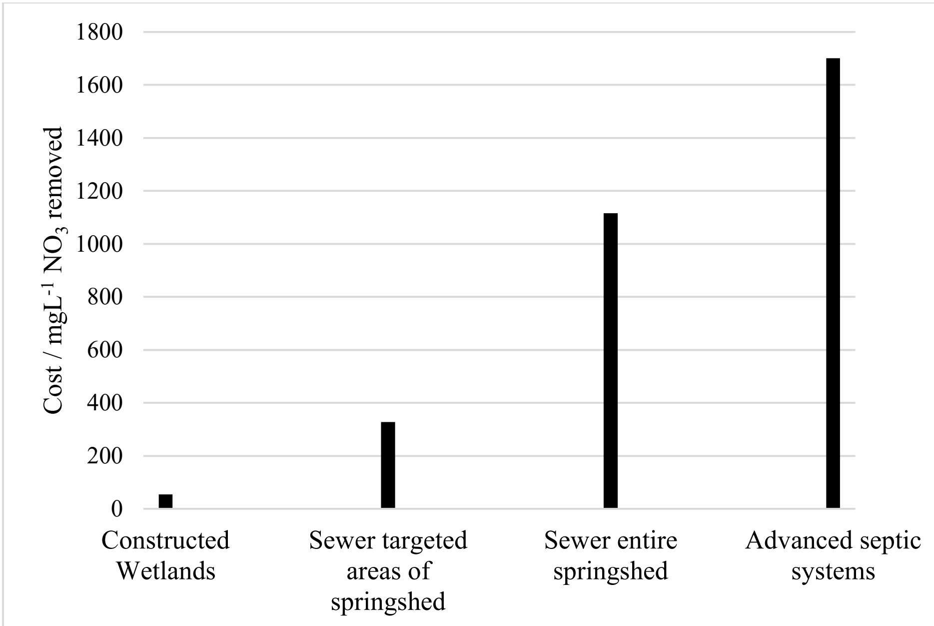
The four nitrogen management scenarios evaluated in this study include a complete and targeted sewer retrofit to a conventional gravity sewer collection system, conversion of existing septic systems to advanced septic systems, and the addition of constructed wetlands. The preliminary conceptual opinion of probable construction cost (estimate) for each scenario involve site preparation (including septic system removal), construction, and, if necessary, treatment plant expansions. This estimate is preliminary and does not include costs associated with design, permitting, percolation ponds, land acquisition, impact fees or operation. The estimate of each nutrient reduction scenario is presented in Table 12. In Figure 18, the ratio of preliminary conceptual opinion of probable construction cost per mg/L of nitrate removed in a twenty-year projection is presented, where nitrate removed is calculated as the difference between each respective scenario and the “do-nothing” scenario.

Table 12: Preliminary conceptual opinion of probable construction cost of nitrogen management scenarios

Scenario	Associated activities	Qty.	Unit Price	**Total (million $)**
Sewer entire springshed area[a]	WWTF expansion Sewer retrofit to conventional gravity sewer collection system consisting of gravity sewer, manholes, force mains, lift stations, sewer service connections, and roadway restoration, not including impact fees.	4,781,514 gallons 25,500 connections	$10 $20,000	**$560**
Conversion of conventional septic systems to advanced septic systems[b,c]	Convert approximately 25,500 septic systems to advanced septic systems	25,500 connections	$10,000	**$255**
Sewer targeted areas of springshed[c]	WWTF expansion Sewer retrofit to conventional gravity sewer collection system consisting of gravity sewer, manholes, force mains, lift stations, sewer service connections, and roadway restoration, not including impact fees.	1,400,112 gallons 7,497 connections	$10 $20,000	**$164**
Constructed wetlands[d,e]	Construction associated with approximately 1,190 acres of constructed wetlands to treat 20 MGD. This cost does not include land acquisitions, design, pipes, or pumps.	14.8 MGD	$547,742	**$8**

Note: The cost estimates provided herein are preliminary and contain error including, but not limited to, the standard error provided in modeled results.

[a]Based on Carroll (2005)
[b]Based on Quentin L. Hampton Associates, Inc., City of DeLand Wastewater & Reclaimed Water Master Plan Update, unpublished report
[c]Based on Spear (2014)
[d]Based on BLS (2016)
[e]Based on Sees (2014)



Note: The cost estimates provided herein are preliminary and contain error including, but not limited to, the standard error provided in modeled results.

Figure 18: Cost to benefit ratio of nitrate management scenarios after a twenty-year projection period.

Discussion and Conclusion

Results of utilizing MODFLOW-2000 and MT3D to simulate nitrate transport within the karst springshed surrounding VBS yielded calibration and validation RMSE values of 0.17 and 0.20 mg/L, respectively. The numerical simulations of the scenarios evaluated here indicate that septic tank removal is the single most effective strategy in the decline of nitrate in groundwater and spring discharge. It is estimated that in 100 years (year 2115), the removal of the septic systems will result in 17% less nitrate at VBS than the removal of 8,000 or less septic systems. Both advanced septic systems and constructed wetlands offer appreciable nitrate removal, however, their efficiency is limited to proper operation and maintenance (Kadlec 2012; Roeder & Ursin 2013).

A preliminary conceptual opinion of probable construction cost of each scenario was compared on the basis of estimated cost per mg/L of nitrate mitigated. Although several assumptions were made that exclude the cost associated with design, permitting, land acquisition, among others, the implementation of constructed wetlands and targeted sewer retrofit appears to have the greatest cost to benefit ratio of each scenario evaluated.

The main objective of this study was to produce a three-dimensional numerical CFT model capable of simulating nitrogen management scenarios for pollution prevention planning of wastewater discharges. The assumptions made herein are adequate for the general purposes of this research, but when simulating projections, flow and concentrations do not transport as darcian and multi-nodal transport is not accounted for. The cost estimates provided herein are preliminary and contain error including, but not limited to, the standard error provided in modeled results. The model relied on recharge, initial concentrations, porosity, dispersivity, and reaction parameters to simulate transport phenomena. Karst matrix and conduit propensities were represented at sinkhole locations (Reed, Wang, Duranceau 2015). The nitrate model was calibrated and validated with nitrate observations collected directly from the VBS vent, seven groundwater wells, ten septic tanks, and five wastewater treatment facilities within the VBS springshed. This work is novel in that 1) it is the first three-dimensional nitrate transport model of a central Florida spring; and 2) it is the first CFT model used to simulate nitrate management scenarios within a karst aquifer in Florida.

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CHAPTER SIX: CONCLUSIONS

From Chapter Two of this dissertation, unique boron isotopic signatures were found in treated wastewater (2.2–15.3‰), fertilizer (21.0‰), local limestone freshwater (40.0‰), and Volusia Blue Spring (VBS) discharge (28.4–45.9‰). Our findings indicate that VBS discharge is currently a varying mixture of limestone freshwater, relict seawater, and anthropogenic recharge. From the results of this study, it can be implied that the anthropogenic boron and nitrate in the spring's vent in the year 2015 is caused primarily by septic systems with some treated wastewater influence.

From Chapter Three, it was found that in septic tank supernatant, nitrate-nitrogen isotopes ranged from +1.25‰ to +10.00‰ and boron isotopic signatures ranged from +8.8‰ to +31.3‰. Nitrate-oxygen isotopes ranged from -3.23‰ to +19.96‰ and were indicative of an anoxic environment. On average, residential septic tanks were found to contain 96 μg L-1 total boron and 63 mg L-1 TKN. This research has shown that the chemical and isotopic content of septic tank supernatant discharge directly contributes anthropogenic boron and nitrogen to the environment.

From Chapter Four, a three-dimensional contaminant fate and transport model, utilizing MODFLOW-2000 and MT3DMS, was developed and calibrated against field observed water levels, spring discharge, and field observed boron. The calibrated VBS model yielded a root-mean-square-error value of 1.8 m for head and 17.7 μg/L for boron concentrations within the springshed. Model results show anthropogenic boron from surrounding urbanized areas contributes to the boron in the spring's vent. From 2015 simulated results, it appears that septic systems and wastewater treatment facilities just east and southeast of the VBS vent are the primary sources of current anthropogenic boron within the VBS springshed. This work is novel in that 1) it is the first

three-dimensional boron transport model of a karst aquifer in Florida; and 2) it is the first CFT model of a central Florida spring.

From Chapter Five, a three-dimensional nitrate fate and transport model, utilizing MODFLOW-2000 and MT3DMS, was developed and calibrated against field observed water levels and field observed nitrogen data from treated wastewater discharge, septic tanks, and fertilized areas. The calibrated VBS nitrate model yielded a root-mean-square-error of 0.17 mg/L throughout the springshed and a 13.6% difference between observed and modeled nitrate concentration at spring discharge. From simulation results and a preliminary conceptual opinion of probable construction cost, it was determined that constructed wetlands and targeted septic system removal are the two most cost effective nitrate management scenarios. The numerical simulations of the scenarios evaluated here indicate that septic tank removal is the single most effective strategy in the decline of nitrate in groundwater and spring discharge. Septic system removal results in the greatest benefit with an estimated 36% nitrate decrease in a forty-year projection of discharge water quality. This work is novel in that 1) it is the first three-dimensional nitrate transport model of a central Florida spring; and 2) it is the first CFT model used to simulate nitrate management scenarios within a karst aquifer in Florida.

APPENDIX: SUMMARY OF ANALYTICAL METHODS

Table A- 1: Summary of Analytical Methods Used for Characterization of Water Samples

Test	Method Reference Number (Standard Method); Instrument	Method Reporting Level (MRL)	Method Detection Level goal (MDL)	Accuracy % Recovery	Precision % RPD	Hold time (HT)	Minimum Sample Vol. (SV)	Cont. Type (CT)[1]	Preservative
Boron	EPA 200.7 / SM: 3120 B. Inductively Coupled Plasma (ICP) Method/Inductively Coupled Plasma Spectrometer	0.005 mg/L	0.005 mg/L	80-120%	<20%	180 days	250 mL	Plastic (Borosilicate glassware should be avoided)	Cool, 4°C; Acidify with 2% concentrated HNO_3 to pH < 2
Boron Isotope	(Hemming and Hanson, 1994): Negative ion mode in Thermal Ionization Mass Spectrometer	0.001 mg-B/L	0.001 mg-B/L	80-120%	+/- 1.0‰	180 days	2000 mL	Plastic	Filter 0.45micron cellulose acetate filter or equivalent; Preservative should be avoided; Chilling not required
Conductivity	2510B. Laboratory Method; Fisher Scientific Traceable Conductivity, Resistivity and TDS Meter	N/A	N/A	N/A	<5	28 days	125 mL	Glass	Cool, 4°C
Nitrate	EPA 300.0 / SM: 4110 B. Ion Chromatography (IC) with Chemical Suppression of Eluent Conductivity	0.01 mg/L as N	0.027 mg/L as N	90-110%	<20%	48 hours	500 mL	Plastic or Glass	Cool, 4°C
Nitrogen Isotope	USGS RSIL Lab Code 2900: Isotope ratio mass spectrometer using denitrifier method	0.07 mg-N/L	0.02 mg-N/L	80-120%	≤0.3‰	180 days frozen	50 mL	Nalgene	Filter 0.45micron nylon filter; preservative should be avoided. Freeze after filtration and ship frozen.
pH	SM: 4500-H+ B. Electrometric Method/ HQ40d Portable pH, Conductivity and Temperature Meter	0.01 units	0.01 units	N/A	±0.1 pH unit	0.25 hours	125 mL	Plastic or Glass	Analyze immediately
Temperature	SM: 2550 B. Laboratory Method/ HQ40d Portable pH, Conductivity and Temperature Probe	0.1 °C	0.01 °C	N/A	NIST approved	0.25 hours	125 mL	Glass / Plastic	Analyze immediately
Total Kjeldahl nitrogen (TKN)	Semi-automated colorimetry; EPA Method 351.2					28 days	250 mL	Plastic	Cool, 4°C; Acidify with 2% concentrated H2SO4 to pH < 2

Table A- 1: Summary of Analytical Methods Used for Characterization of Water Samples

Test	Method Reference Number (Standard Method); Instrument	Method Reporting Level (MRL)	Method Detection Level goal (MDL)	Accuracy % Recovery	Precision % RPD	Hold time (HT)	Minimum Sample Vol. (SV)	Cont. Type (CT)[1]	Preservative
Turbidity	SM: 2130 B. Nephelometric Method	0.020 NTU	0.012 NTU	N/A	<10%	48 hours	100 mL	Plastic/ Glass	For best results, analyze immediately without altering sample; If storage is required, cool to 4°C.

Table A- 2: Summary of Field Analytical Methods

Test	Method Reference Number (Standard Methods); Instrument	Range / Resolution	Calibration Procedures
Conductivity	LaMotte Con 5 Field Probe (with temperature compensation)	0 – 20 mS Range 1 µS resolution	Calibrated against manufacturer's internal method and frequent membrane inspection
Dissolved Oxygen	YSI 550A Sensor	0 – 50 mg/L O_2 Range	Calibrated against manufacturer's internal method and frequent membrane inspection
pH	LaMotte pH 5 Series Field probe (with temperature compensation)	0 – 14 Range, 0.01 resolution	Commercial pH calibration buffers, pH 4, 7, 10. Calibrated prior to analyzing any batch of samples using 2 point calibration with standard buffers
Temperature	Mercury-filled Celsius Thermometer	0 – 100 ºC range; 0.1 ºC resolution	Calibrated against NIST-certified thermometer
Turbidity	SM: 2130 B. Nephelometric Method; HACH 2100q Portable Turbidimeter	0.02 – 200 NTU	Calibrated against using 0.1, 10, 20, 100, 200, and 800 NTU standards

SM = Standard Methods