MEASURING AND MODELING WATER AND NUTRIENT FLUX BETWEEN A MID-MISSOURI STREAM AND FORESTED RIPARIAN ZONE IN THE CENTRAL U.S.

A Dissertation presented to

The Faculty of the Graduate School

University of Missouri-Columbia

In Partial Fulfillment of the Requirements for the Degree

Doctor of Philosophy

By

Pennan Chinnasamy

Dr. Jason A. Hubbart, Dissertation Supervisor

DECEMBER 2012

The undersigned, appointed by the dean of the Graduate School, have examined the dissertation entitled

MEASURING AND MODELING WATER AND NUTRIENT FLUX BETWEEN A MID-MISSOURI STREAM AND FORESTED RIPARIAN ZONE IN THE CENTRAL U.S.

presented by **Pennan Chinnasamy**

a candidate for the degree of

Doctor of Philosophy

and hereby certify that, in their opinion, it is worthy of acceptance.

Dr. Jason A. Hubbart

Dr. Stephen H. Anderson

Dr. Shibu Jose

Dr. Chung-ho Lin

Dr. Allen Thompson P.E.

DEDICATION

ஆரறிவு மானிடனாய் பிறக்கவைத்தாய்,
உயிரினிலும் மேலான பெற்றோர்களை அருளினாய்,
நல் உறவும் நட்பும் புடைசூழ பாலித்தாய்,
ஆதிபகவானே,
நீ யமக்கருளிய சுடர்மிகு அறிவை,
பாரும், சக உயிரும் நலம் வாழ, பயனுற,
அருள்வாயாக.

Thou blessed me to take human birth,
To my loving parents on earth,
And positioned me amongst good people,
Thank you Lord, please
Bless me with the strength to use,
Thy gifts of knowledge and wisdom,
To benefit all living forms of Thy Kingdom.

To the ***CREATOR****, from the created.*

ACKNOWLEDGMENTS

First and foremost, I would like to thank all the Gods, across all religions, language and across all boundaries, for supporting me from my first breath and will support me through the last and beyond. Next to God, I would like to thank my family members for their sacrifices for me and for supporting me in all my journeys and future endeavors till my departure. My deepest gratitude goes to my parents. Particular thanks go to my mother for her hard work in raising me, single handedly after my father passed away when I was seven, and for her unconditional love and support all through my life – without her hard work and sacrifice I am nothing.

I would like to thank all my committee members for their constant encouragement, patience, support and willingness to share knowledge and expertise, without which I could not have matriculated. I would like to especially thank my adviser, and Director of the Interdisciplinary Hydrology Lab (IHL), Dr. Jason A. Hubbart, for his willingness to accept me in his lab and for his guidance and patience in allowing me to get accustomed to a new field in my career. I am extremely grateful to him for constantly pushing me to explore my capabilities and inner strengths. I also would like to thank Dr. Hubbart for his confidence in me and for improving my writing style.

Sincere thanks to my committee members, Drs. Stephen H. Anderson, Shibu Jose, Chung-ho Lin and Allen Thompson. Special thanks go to Dr. Anderson and Dr. Jose for meeting with me and for often enquiring about my progress and for constant support.

Special thanks to Dr. Lin for having tremendous confidence in me and for acknowledging my passion. Special thanks to Dr. Thompson for his discussions related to the project.

Sincere thanks are due to Dr. John M. Kabrick for many scientific discussions and for helping me when preparing for my comprehensives. I would like to thank all the faculty of the Forestry, Geology, Geography and the Soil, Environmental and Atmospheric Sciences departments for their support and encouragement and to all the faculty of the University of Missouri who have instructed me in my coursework.

I would like to thank all the IHL members for their support in instrumentation and fieldwork. This has been a field work intensive research project, and I would have not been able to collect all of the data that I have without the help of others, including, but not limited to, Ed Bulliner, Graham Freeman, Gregory Hosmer, Charles Keatings, Greg Brostoski, Jerod Romine, Gabe Waterhouse, Joe Sheals, John Nichols, Amanda Wolfgeher, and Michael Hullinger. My sincere thanks go to Dr. Stephen G. Pallardy and Mr. Kevin P. Hosman for providing climate reference data from their project at Baskett. Special thanks to Kevin for hauling the field truck out a couple of times when I got stuck in the field.

I would like to thank all my friends in India, U.S. and other parts of the world for their encouragement, support and well wishes. I would love to name them all, but you know who you are. Most of these friends will be with me forever.

I extend gratitude to The United States Environmental Protection Agency (EPA) Region 7 (Grant Number: CD-97701401-0) for funding the project.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

ABSTRACT

Few studies have investigated spatiotemporal variations of surface water (SW) – groundwater (GW) interactions (including both hydrologic and nutrient) in the central U.S. Therefore, understanding of riparian zone and stream connectivity is limited in that region. Accurate characterizations of SW-GW interactions will improve process based understanding, which is critical for management and outcome predictions of management scenarios. To improve process based understanding of SW-GW interactions, high-frequency water quantity data (stream flow, groundwater flow and precipitation) were collected (5-min intervals) from four stilling wells and two transects of piezometers (n = 6 each) during the 2011 water year along Brushy Creek, located in Boone County, central Missouri. Weekly water quality data (nitrate (NO_3^-), total phosphorous (P), potassium (K) and ammonium (NH_4^+) were also collected from stream (n = 4) and piezometers (n = 12). Results indicate that Brushy Creek alternates between being a losing and gaining reach, along the study reach (length = 830 m), but is on average a losing stream (-3 x 10^{-5} m^3 s^{-1} m^{-1}), with a loss of 28 and 7% of total surface flow to groundwater during winter and spring, respectively. Based on established assessment criteria, GW modeling performance with HYDRUS – 1D was deemed '*Very good*' (NS = 0.95, r^2 = 0.99, RMSE = 2.38 cm and MD =1.3 cm) and should therefore be used by land managers with confidence to predict riparian zone water storage and flow. Annual average SW NO_3^- was 0.53 mg L^{-1}, while P, K and NH_4^+ concentrations were 0.13, 3.29 and 0.06 mg L^{-1}, respectively. Nine

meters from the stream, annual average concentration for GW NO_3^- was 0.01 mg L^{-1}, while total P, K and NH_4^+ concentrations were 0.03, 1.7 and 0.04 mg L^{-1}, respectively. Results of a hyperbolic model, used to quantify hydrological controls on stream water nutrient concentrations, indicated that NO_3^- and K exhibited dilution behavior while NH_4^+ had a concentration effect and P was hydrologically constant. Spatial variations in SW nutrient concentrations varied significantly ($p < 0.01$), while GW concentrations were not significantly different between sites ($p > 0.05$). Shallow GW modeling with MODFLOW provided numerical approximations of hydrologic and nutrient flux, that are comparable (NS = 0.47, r^2 = 0.77, RMSE = 0.61 cm and MD =0.46 cm) to field observations. Study results indicate that karst geology promotes rapid water movement that can increase dominance of shallow-groundwater geochemical nutrient cycling pathways (e.g. weathering and transport) relative to biochemical nutrient cycling pathways (e.g. plant uptake and N-fixation). Baseline data and results of analysis presented in this dissertation will aid in identification, improvement and validation of management tools that will contribute to advancements in stream - riparian zone best management practices, in particular in karst hydrogeological environments.

CHAPTER I: MEASURING AND MODELING WATER AND NUTRIENT FLUX BETWEEN A MID-MISSOURI STREAM AND FORESTED RIPARIAN ZONE IN THE CENTRAL U.S.

1.1. Introduction

Surface water features like springs, streams and rivers interact with groundwater through complex physical processes (Winter *et al*., 1998). Stream water passes between the active channel and subsurface thus interacting with shallow groundwater (Jones and Mulholland, 2000). Due to tightly coupled exchange processes for water and nutrients between stream and shallow groundwater, many plants, animals, insects and fish inhabit the stream and the land adjacent to the stream (i.e. the riparian zone). Streams and adjacent riparian zones thus provide habitat for flora and fauna, and serve as recreational area for camping, fishing, hunting, and boating (Crimo and Mc Donnell, 1997; Lins and Slack, 1999; Jones and Mulholland, 2000; USEPA, 2000; Harvey and Wagner, 2000). Nutrients including nitrogen, ammonium and phosphorus are critical to sustain all the aforementioned stream water uses (Stanley and Jones, 2000). It is therefore important to have a process understanding of water and nutrient dynamics in the stream and adjacent riparian zone to manage the resource. Previous studies of land-water interactions indicated that stream riparian zones serve as critical interfaces for nutrients between terrestrial and aquatic environments (Bencala, 1984; Gilliam, 1994; Crimo and Mc Donnell, 1997; Jones and Mulholland, 1998; Lins and Slack, 1999; Jones and Mulholland, 2000; Martí *et al*., 2000; Akerman and Stein, 2008). However, there remains an ongoing need for information to improve management outcomes. In particular, limited research has been conducted in the Ozark border forest region of the central U.S., where integrated process-based studies linking hydrologic flowpaths with nutrient and biological status is warranted to provide improved understanding of riparian zone regulation of stream nutrient concentrations (Hill, 2000).

1.2 Statement of need

Advances in riparian zone management require innovative reach-scale experimental studies that will result in improved management tools (e.g. models) (Sophocleous, 2002). Aside from lacking quantifiable validation, riparian zone management formulation and associated management practices seldom take into account water and nutrient dynamics between stream water and shallow groundwater (Jones and Mulholland, 2000; Burt *et al*., 2010; Levia *et al*., 2011). This is the case for riparian zone management plans in the forested regions of Mid-Missouri, U.S., where karst geological associations may result in greater hydrologic and nutrient interaction complexity between the stream and riparian zone shallow groundwater. Studies are warranted that will quantify subsurface interactions between the surface water (SW) and shallow groundwater (GW) in the adjoining forested riparian zones in Missouri to improve confidence of current management practices. In addition, investigations of spatiotemporal variations in stream water – groundwater interactions is necessary to increase process based understanding of water and nutrient dynamics between terrestrial and aquatic ecosystems. Improved process based understanding can then be used to validate and improve numerical models to predict future stream water-shallow groundwater interactions.

1.3. Research Objectives

The objectives of the following dissertation research were to use a heavily instrumented nested-scale study design to investigate shallow GW flow of a forested riparian zone of a mid-Missouri stream in order to: (a) Quantify spatiotemporal variations in hydrologic flux; (b) Quantify spatiotemporal variations in nutrient concentration (i.e. Nitrate, Potassium, Phosphorus and Ammonium) dynamics; and (c) Use MODFLOW and HYDRUS 1D to predict hydrologic and nutrient flux, and compare modeling outputs to observations by means of statistical analyses.

1.4. Hypotheses

This research will quantify hydrologic and nutrient concentration flux between a Mid-Missouri stream and adjacent forested riparian zone.

The following hypotheses will be evaluated:

- H1o: Hydrologic flux between the stream and an adjacent forested riparian zone will have spatial and temporal dependence.
- H1a: Hydrologic flux between the stream and an adjacent forested riparian zone will not have spatial or temporal dependence.
- H2o: Nutrient concentration fluxes (concentration levels of Nitrates, Potassium, Phosphorus and Ammonium) between a stream and an adjacent riparian zone are bi-directional in nature and will vary significantly spatially and temporally.
- H2a: Nutrient concentration fluxes (concentration levels of Nitrates, Potassium, Phosphorus and Ammonium) between a stream and an adjacent riparian zone are not bi-directional in nature and will not vary significantly spatially and temporally.
- H3o: MODFLOW (along with sub-modules) and HYDRUS 1D can accurately predict hydrologic flux and nutrient concentration between a stream and adjacent forested riparian zone.
- H3a: MODFLOW (along with sub-modules) and HYDRUS 1D cannot accurately predict hydrologic flux and nutrient concentration between a stream and adjacent forested riparian zone.

1.5 Background

1.5.1 Stream water – shallow groundwater hydrologic interactions

Stream flow represents an integration of complex physiographic conditions exerting control over many important stream processes including volume, current velocity, channel geomorphology and substrate stability, as well as habitat (Poff and

Ward, 1989). To better understand factors influencing quality and quantity of stream water, it is critical to understand streamflow processes to quantify transported material exchange (Wood *et al*., 2007). Significant hydrologic exchange between shallow groundwater and streams should exact a strong influence on nutrient cycling rates (Duff and Triska, 2000; Hendricks and White, 2000). Thus quantifying shallow groundwater flow is primary requisite for understanding SW-GW hydrologic interactions.

Shallow groundwater flow can be determined using various methods including Darcy-groundwater flow calculations and tracer tests that quantify the transport of an introduced solute (Jones and Mulholland, 2000). Other methods include naturally occurring environmental tracers such as water temperature or specific conductivity, and direct measurements of groundwater exchange using devices such as seepage meters (Levia *et al*., 2011). Harvey and Bencala (1993) used numerical models to show groundwater flux of 1.6×10^{-6} m^{-3} s^{-1} m^{-1} at St. Kevin Gulch in Colorado, demonstrating stream-groundwater exchange processes influenced by streambed and stream slope variability. Castro and Hornberger (1991) utilized solute tracers in North Fork Dry Run, Virginia, to show that 47% of total catchment water yield was shallow groundwater. Mulholland *et al*. (1997) used seepage meters to show that groundwater flow towards the stream was 2.2×10^{-4} m^3 s^{-1} at Walker Branch Creek in North Carolina. While many methods to estimate shallow groundwater exist, a great deal of research is needed to improve the understanding of groundwater regimes. Dahm *et al*. (1998) concluded that spatiotemporal variations in stream-groundwater exchange processes require investigation in varying geological settings to advance predictive modeling. Sophocleous (2002) emphasized the need for a comprehensive hydrogeoecological framework to better-understand groundwater exchange in relation to land use, geology and biotic factors.

In recent years, many studies utilize a Darcian approach (Darcy, 1856), that uses saturated hydraulic conductivity to quantify groundwater flow (McDonald and Harbaugh, 1988; Levia *et al*., 2011; Jones and Mulholland, 2000a). However, shallow groundwater flow is not limited only to the saturated zone. Hence, advanced groundwater models, such as HYDRUS – 1D, use variably saturated hydraulic conductivity (Richards, 1931) and can thus simulate both saturated and unsaturated groundwater flow (Šimůnek *et al*. 1998, 1999, 2008; Ramos *et al*. 2011; Luo and Sophocleous, 2010). Freely available HYRDUS – 1D has been shown to effectively quantify stream-riparian zone hydrologic connectivity. Luo and Sophocleous (2010) used HYDRUS-1D to estimate groundwater flow values ranging from -3.5 x 10-8 to 3.5 x 10-8 m s^{-1} with a coefficient of determination (r^2) value of 0.75 between simulated and measured groundwater flow in an agricultural field located in Shandong province, China. Even though numerical methods can estimate GW flow, studies that integrate in-situ field and modeling methodologies are necessary to advance quantitative understanding and consequently management of groundwater resources (Dahm *et al*. 1998; Sophocleous, 2002; Burt *et al*., 2010; Levia *et al*., 2011).

1.5.2. Stream water – shallow groundwater nutrient concentrations

Of the many nutrients transported by stream waters, Nitrogen and Phosphorus are major influences of primary productivity in streams (Mulholland and Webster, 2010).

Few researchers have studied the spatial and temporal variations of nutrients along hydrological pathways, such as unsaturated or saturated zones and vertical and lateral water movement through the riparian zone (Triska *et al*., 1989; Findlay *et al*., 1995; Jones *et al*., 1995).

A study by McClain *et al*. (1994), in a central Amazon watershed, showed that nitrate (NO_3^-) concentration decreased from 650 to 50 μg L^{-1} after passing through the riparian subsurface, whereas ammonium (NH_4^+) increased from 150 to 600 μg L^{-1}. Study results indicated that some nutrients (such as NO_3^-) are removed in the riparian zone while other nutrients (such as NH_4^+) can be leached from subsurface soils due to the movement of GW. In a study conducted on GW of the riparian zone of a Puerto Rican rain forest, Mc Dowell *et al*. (1992) observed nutrient concentrations upland of the riparian zone buffer, and noted a decrease in NO_3^- of 500 to 9 μg L^{-1}, and an increase in the NH_4^+ concentration from 30 to 500 μg L^{-1}, exhibiting similar trend to the study by McClain *et al* (1994). Rapid declines in the NO_3^- concentration between uplands and riparian zones have been noted in many forested and grass riparian areas (Lowrance *et al*., 1984; Peterjohn and Correll, 1984; Haycock and Pinay, 1993). PeterJohn and Correll (2009) estimated that a 50 m riparian forest buffer in Maryland removed 11 kg of organic nitrogen, 0.83 kg of NH_4^+, 2.7 kg of NO_3^-, and 3 kg of total P over a one year period, indicating the need to couple riparian forests and managed habitats in order to reduce diffuse pollution. Niyogi *et al*. (2010) noted seasonal variations in stream water average nutrient concentration levels (300 and 0.91 μg m^{-2} s^{-1}during the fall and summer, respectively) within a 10 km study reach in Mill Creek, Missouri, indicating the need to quantify seasonal variations of in-stream nutrient concentrations to preserve stream water quality. According to a 20 day (d) study by Triska *et al*. (1989) stream water accounted for more than 88% of flow in piezometer wells less than four meters from the wetted stream channel and the lowest percentage of stream water was 47% at a well ten meters from the stream. Coupled NO_3^- concentration increased from 75 μg N L^{-1} –130 μg N L^{-1} indicating that the variations in lateral extent of SW-GW flow can also influence nutrient cycling processes in the GW of the riparian zone (Triska *et al*., 1989). Hill (1996) reviewed NO_3^- concentration findings from 20 watersheds concluding that 70% of riparian zones had NO_3^- concentrations that were 90% lower than those in the stream. Hill (1996) further reported that the current uncertainties in understanding riparian zone shallow groundwater nutrient cycling stem from an inadequate understanding of the hydrologic regime, stressing the need for research in varying landscape hydrogeology and climates including additional nutrients (e.g. phosphorous, potassium, and ammonium).

Studies that successfully quantify surface water and shallow groundwater (SW-GW) nutrient concentration relationships can provide information that will aid riparian forest management practices by identifying seasonal variations in stream nutrient loading (Burt *et al*., 2010) and help predict water quality alterations subsequent to specific management scenarios (Levia *et al*., 2011; Jones and Mulholland, 2000). SW-GW nutrient studies can also aid in the formulation of management plans for preventing excess stream nutrient loading (e.g. by adjusting riparian zone buffer width), and in preventing excess nutrient leaching (e.g. by installing drainages for excess riparian zone water that can increase nutrient leaching). Due to nutrient concentration estimations in previous studies that employed advancements in scientific tools and numerical models (Levia *et al*., 2011), reliable science-based riparian zone management plans are often possible. However, SW-GW nutrient studies remain limited in many regions, including the central mid-western region of the U.S., particularly in Ozark border forested ecosystems. Kirchner *et al*. (2004), Jones (2007), and Cassidy and Jordan (2011) showed the failure of coarse sampling approaches for estimating nutrient loading in SW-GW interactions, thereby indicating the need for higher resolution (spatial and temporal) studies. Given the aforementioned needs, the following work uses high-frequency water quality monitoring in an Ozark bordered forest to quantify spatiotemporal variations in SW-GW nutrients (NO_3^-, total P, K and NH_4^+).

1.5.3. Modeling stream water – shallow groundwater interaction

Effective watershed management requires modeling tools that provide a scientific basis for decision-making and problem solving. Hydrologic models that incorporate climate, topography, geology land-use and land cover are vital for accurately simulating water flow (NRC 1999). Hydrologic models range from simple index based models to complex physically process based models. Simple index models may lack physical basis to accurately predict the spatial and temporal distribution of SW-GW exchange. Spatial and temporal distribution of SW-GW exchange is important for quantifying nutrient flux. Simple index models often do not have the ability to take into account the effects of heterogeneity (such as topography, soil type, soil porosity and hydraulic conductivity) over the entire watershed. The flexibility of simple index modeling is largely due to assumptions of soil homogeneity, isotropy, simple geometry (in assuming flow paths) and simple initial conditions whereas the real system could be heterogeneous, anisotropic and have complex geometry and antecedent conditions (Packman *et al*., 2000).

Numerical models use fundamental governing equations (physics-based) to predict future water fluxes and resident times (Cardenas, 2008). Physically-based numerical modeling places strenuous demands on both the modeling platforms and the quality and quantity of data necessary to run the models (Moore *et al*., 1993). Physically based models are complex models that take into account dominant physical processes (i.e. hydrologic fluxes, climate and precipitation). Advantages of physically- based models include that modeling results calibrated with data from well-instrumented sites can be applied to other sites of interest (Lautz and Siegel, 2006). Numerical groundwater flow models use 2D (two dimensional) or 3D (three dimensional) spatial discretization of the area to be simulated (Wondzell *et al*., 2009). Compared to 2D transient storage models, 3D groundwater flow models have much more intensive data requirements. According to Harvey and Wagner (2000), hydrologic fluxes across forested riparian streambeds could be calculated based on two-dimensional contour maps of hydraulic head and the basic governing equations of ground flow. Therefore, even though 3D models can give more accurate results than 2D models, when limited data is available 2D or 1D models can be sufficient to improve physical process understanding.

Groundwater flow models range from simple stage index based models to complex physical process based models. Computer simulated numerical models have been widely used in sites with varying geologic settings. In recent years many researchers (e.g. Wroblicky *et al*., 1998; Storey *et al*., 2003; Kasahara and Wondzell, 2003; Jones and Mulholland, 2000; Simunek *et al*., 2008, 1998; Ramos *et al*., 2011) have used numerical models (e.g. MODFLOW, CPFLOW, SUTRA, HYDRUS) to understand SW-GW interactions. One of the most widely used models is MODFLOW (Sophocleous, 2002) McDonald and Harbaugh, 1988). MODFLOW, first released in 1984, is currently the most commonly used numerical model used by the U.S. Geological Survey for groundwater flow simulations (Harbaugh and McDonald, 1996a and 1996b; Harbaugh *et al*., 2000). In addition to simulating ground-water flow, the scope of MODFLOW in recent years has been expanded to include solute transport and particle tracking (Harbaugh *et al*., 2000).

To quantify stream water - groundwater water exchange, many studies utilize a Darcian approach (Darcy, 1856) utilizing an estimated saturated hydraulic conductivity (McDonald and Harbaugh, 1988; Jones and Mulholland, 2000a; Levia *et al*., 2011). Advanced groundwater models, such as HYDRUS – 1D, use variably saturated hydraulic conductivity (Richards, 1931) and can thus simulate both saturated and unsaturated groundwater flow (Šimůnek *et al*., 1998, 1999, 2008; Ramos *et al*., 2011). HYRDUS – 1D, free to public, has been shown to effectively quantify stream-riparian zone hydrologic connectivity. Luo and Sophocleous (2010) used HYDRUS-1D to estimate groundwater flow values ranging from -3.5 x 10-8 to 3.5 x 10-8 m s^{-1} with a coefficient of determination (r^2) value of 0.75 between simulated and measured groundwater flow in an agricultural field in Shandong province, China. A number of numerical groundwater models have been shown to successfully predict vertical surface – subsurface interactions, however, scientists note that improved model accuracy requires proper parameterization, emphasizing the need for higher resolution (spatial and temporal) field observations (Hurst *et al*. 2004; Katsuyama *et al*. 2009). Shallow groundwater flow studies that integrate in-situ field and modeling methodologies are necessary to improve quantitative understanding and consequently management of groundwater resources (Dahm *et al*. 1998; Sophocleous, 2002; Akerman and Stein, 2008; Abesser *et al*. 2008).

1.6. Study Site and Instrumentation

This research was conducted on two reaches of Brushy Creek within the Thomas S. Baskett Wildlife Research and Education Area (BREA), located in the Ozark border region of south-central Missouri, U.S. (Pallardy *et al*., 1988) (Figure 1.1.). The BREA is a wildlife reserve that has been managed by the University of Missouri since 1938 (Rochow, 1972). Aldo Leopold dedicated the BREA, initially known as the Ashland Wildlife Research Area (AWRA), on April 26, 1938, giving the keynote address "Whither Missouri" (Leopold, 1938). Through a series of agreements between the land owners (17 at the time) and the 1935 year's Resettlement Administration act (RA, 1935), the AWRA was transferred via a quit claim deed to the University of Missouri in 1960.

Before the RA took over the land, AWRA was comprised of over 1000 acres maintained by 34 owners (census from the year 1875). According to the agricultural census records, in the 1880's Allan Burnett used the floodplain at AWRA to raise livestock and also harvested approximately 300 pounds of maple sugar and 110 apple trees per year. Another farmer, Joseph Zumwalt had similar practices as Burnett and harvested 500 pounds of tobacco per year. According to the 1853 plat book commissioned by James Rollins (the Father of the University of Missouri), the oldest ownership of AWRA dates back to 1827 when Joseph Gordon settled along the floodplain area. In 1988, AWRA was renamed the Baskett Wildlife Research and Education Area (BWREA), now known as the BREA, and is used primarily for conducting research. To date over 150 publications and 100 thesis and dissertations have come from the research work conducted at BREA.

The BREA watershed has not been subject to cutting, harvesting or other major disturbances resulting in the current 60 year old forest. The climate in the BREA is humid-continental (Critchfield, 1966). Mean January and July temperatures are -2.2 °C and 25.4 °C, respectively. Mean annual precipitation is 1,037 mm, as recorded between 1971 and 2010 at the Columbia Regional Airport located 8 km north of the BREA (Belden and Pallardy, 2009). The average annual temperature, from 2005-2010, measured at the on-site Ameriflux tower, was 13 °C; and average precipitation was 930 mm versus 12.9 °C, and 1,089 mm at the Columbia Regional Airport during the same time period. Brushy Creek is a second order stream (Strahler, 1952) with an average slope of 0.94%. Brushy Creek joins Cedar Creek, 4 km south of the BREA, subsequent to the drainage of a watershed of an approximate area of 9.17 km^2.

The BREA’s dominant soils are Weller silt loam and Clinkenbeard clay loam (Rochow, 1972) while the underlying limestone geology is of Ordovician and Mississippian age. Riparian zone soils consist of Cedargap and Dameron soil complexes (USDA soil map unit 66017 from USDA (2009)). The BREA soils are well drained and exhibit an average bulk density of 1.2 to 1.4 g cm^{-3} (Young *et al*., 2001).

Current land use ranges from second growth forests in the southern portion to pastures in the northern portion. The watershed consists of 2.6% suburban land use, 17.9% cropland, 33% grassland, 43.2% forest, and 3.3% open water and wetlands

(USDA, 2009). The BREA's vegetation consists of northern and southern division oak-hickory forest species (Rochow, 1972) including American Sycamore (*Platanus occidentalis*), American Elm (*Ulmus americana*), and Black Maple (*Acer nigrum*) dominate riparian reaches (Belden and Pallardy, 2009). Understory vegetation consists of Sugar Maple (*Acer saccharum*), Flowering Dogwood (*Cornus florida*), and Black Cherry (*Prunus serotina*) (Reed, 2010). Climate data were collected from an AmeriFlux tower, located at an elevation of 238 m, on a forested ridge (Table 1.1. and Figure 1.1.). Flux tower data for the study period (WY 2011) were available from a public ftp server: (ftp://ftp.atdd.noaa.gov/pub/GEWEX/2010/mo/). Precipitation data (measured using a Campbell Scientific Inc. TE525 Texas Electronics rain gauge, with an error of ± 1% for rates up to 2.54 cm hr^{-1}) and air temperature data (measured using a Vaisala HMP45C-L temperature sensor with an error of ± 0.2°C from 0 to 60°C and from ± 0.4°C at -35°C) were downloaded from the aforementioned FTP site in order to compliment this study.

Four in-stream stilling wells were installed (hereafter referred to as SI – SIV) in 2010, in order to estimate stream discharge before and after each piezometer grid (Table 1.1. and Figure 1. 1.). Stilling wells, equipped with Solinst® Levelogger Gold pressure transducers (error ± 0.003 m) were used to record the stream stage at five minute intervals. Streamflow rating curves were determined from measured stage-discharge relationships using the stream cross section method (Dottori *et al*., 2009) with a Marsh-McBirney ® Flo-Mate flow meter (with an error of ± 2%).

Between SI and SII, four piezometers were installed along a transect (Piezometer Site I, hereafter referred to as PZI) that extended from 3 m from the stream edge to 9 m into the riparian zone (Table 1.1. and Figure 1. 1.). PZI was located at 38°44' N latitude and 92°12' longitude at an elevation of 177 m along the east-west stream reach approximately 90 m long and 15 m wide at bankfull. In a similar manner, Piezometer Site II (PZII) was located 660 m S-SE of PZI at 38°43' N latitude and 92°12' W longitude at an elevation of 174 m along an approximate north-south stream reach 157 m long and 10 m wide at bankfull. Each 3.58 m long drive-point piezometer with a 4 cm inner diameter and a 0.76 m slotted screen at the end was equipped with a Solinst® Levelogger Gold programmed to log water level at five minute intervals (Figure 1.2.).

A forest inventory was conducted at PZI and PZII, during the summer of 2011 (July). At each study site, a 100 m^2 (10 by 10 m) study plot was established. Each plot included 25 measurement locations spaced one meter apart in grid fashion. Diameter at breast height (DBH) was collected, from trees within the plot (with dbh > 1 inch), to quantify basal area per acre. The piezometer sites had a basal area of 111 and 218 ft^2 $acre^{-1}$ at PZI and PZII, respectively. The number of stems (with dbh > 1 inch) in a 10 by 10 m plot were collected at PZI and PZII. Forest inventory data indicated that PZI and PZII had 607 and 527 stems per acre respectively. Within each plot, convex and concave densiometers were used to quantify canopy cover. Results using convex densiometer indicated an average canopy cover of 95.6 and 95.8% at PZI and PZII, respectively. Concave densiometer method results indicated a canopy cover of 94 and 95% at PZI and PZII, respectively. Between the months of April and November of 2010, leaf Area index (LAI) was collected by Bulliner (2011), at PZI and PZII, using ceptometers (Decagon Devices LP-80) and using hemispherical photography (using a Nikon D60 digital SLR camera). Average leaf area index (LAI) was 2.64 at PZI, while PZII had 2.43 (Bulliner, 2011). Soil infiltration capacity was measured at the study plots (n = 25) at PZI and PZII, using the double ring infiltrometer method during the summer of 2011 (May). Results indicated an infiltration rate of 182 and 101 mm hr^{-1} at PZI and PII, respectively, indicating rapid movement of water from surface to subsurface layers.

Weekly manually collected (grab) water samples were analyzed for nitrate [NO_3^-], total phosphorous [total PO_4^{3-}], potassium [K] and ammonium-N [NH_4^+] concentrations using a HACH® DR 2800™ spectrophotometer, housed in the Interdisciplinary Hydrology Lab located in the School of Natural Resources at the University of Missouri. A detailed procedure of the aforementioned methods is available at www.hach.com (HACH, 2007).

Table 1.1. Location of stilling wells, piezometer transects and Ameriflux climate tower in Baskett Wildlife Research and Education Area [BREA], along Brushy Creek, central Missouri, U.S.

Site	Latitude °	Longitude °
SI	38.739	-92.208
SII	38.738	-92.206
SIII	38.733	-92.205
SIV	38.732	-92.204
PZI	38.737	-92.207
PZII	38.732	-92.203
Ameriflux	38.744	-92.200

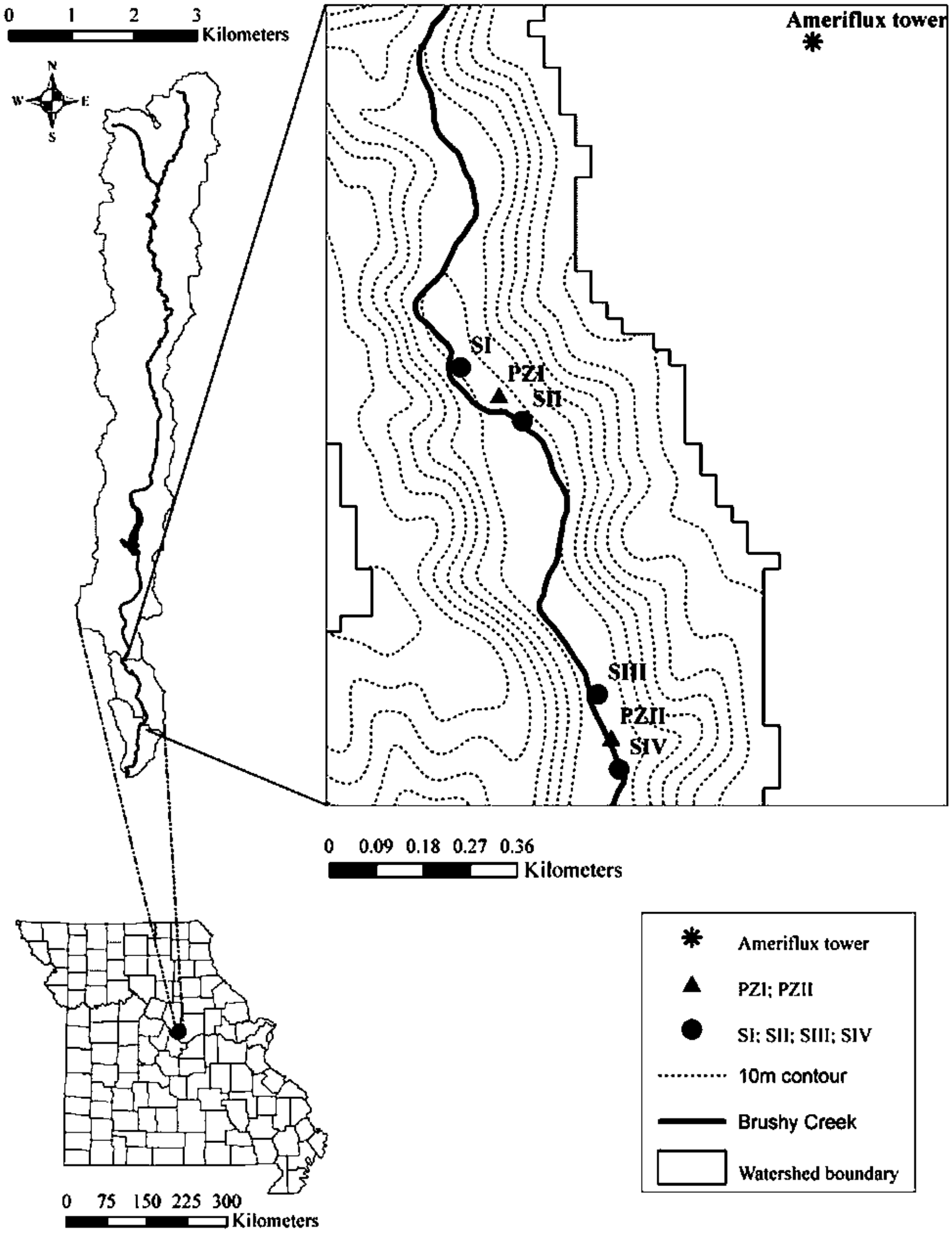

Figure 1.1. Study sites (SI-SIV) and piezometer locations (PZI, PZII) in Baskett Wildlife Research and Education Area [BREA], along Brushy Creek, central Missouri, U.S.

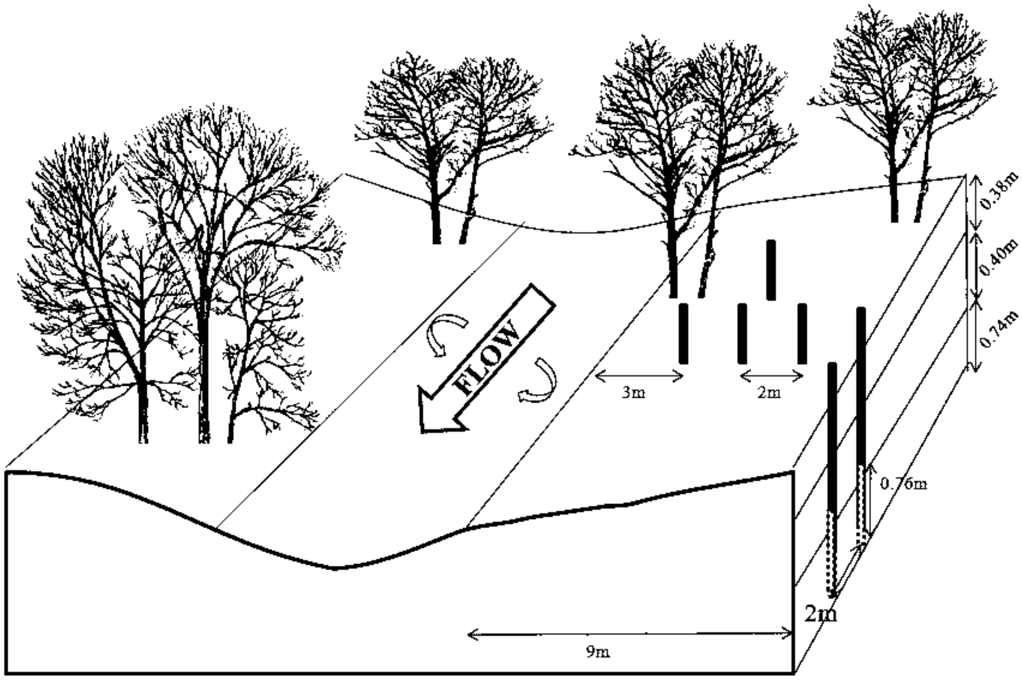

Figure 1.2. Cross section of piezometric array study design in Baskett Wildlife Research and Education Area [BREA], along Brushy Creek, central Missouri, U.S.

1.7. Dissertation structure

This dissertation is presented in the following self-contained chapters: Chapter two, “Measuring and Modeling Shallow Groundwater and Flow Connectivity to a Forested Ozark Border Stream,” uses streamflow data and shallow groundwater head data from the 2011 water year to assess spatiotemporal variations in surface water - groundwater hydrologic interactions. Annual and seasonal groundwater flux rates are quantified. Chapter three, “Quantifying Nutrient Concentrations of Stream and Shallow Groundwater in an Ozark Border Forest of the central U.S.,” uses stream water and shallow groundwater nutrient (nitrate, phosphorous, potassium and ammonium) concentration data to quantify spatiotemporal variations in nutrient concentration and flux between surface water and shallow groundwater. Chapter four, "Modeling Surface water – Shallow Groundwater Interactions in an Ozark Border Stream using MODFLOW", assesses MODFLOW performance, and uses two distinct modules (M3TDMS and MODPATH), each requiring field measurements listed in preceding chapters, to improve Ozark border riparian zone shallow groundwater flow estimations with seasonal variations in a karst geologic setting. M3TDMS is used to quantify spatiotemporal variations in nutrient (nitrate) loading in the shallow aquifer from the surface water. MODPATH is used to estimate spatiotemporal variations in flowpath length and water travel and residence time in the riparian zone. Chapter five, "Conclusions and Synthesis," presents a summary of the key findings of this study and discusses future research directions that will lead to further improved understanding of hydrologic and biochemical responses to forest management in this topographically distinct region of central U.S.

1.8. References

Abesser, C., Wagener, T, and Nuetzmann, G., 2008. Groundwater-Surface Water Interaction: Process Understanding, Conceptualization and Modeling. IAHS Publication, Oxfordshire, UK.

Akerman, D., and Stein, D.E., 2008. Evaluating the Effectiveness of Best Management Practices Using Dynamic Modeling. Journal of Environmental Engineering.

Belden, A. C., and Pallardy, S. G., 2009. Successional trends and apparent Acer saccharum regeneration failure in an oak-hickory forest in central Missouri, USA, Plant Ecol., 204, 305-322, doi: 10.1007/s11258-009-9593-4.

Bencala, K. E., 1984. Interactions of solutes and streambed sediment. A dynamic analysis of coupled hydrologic and chemical processes that determine solute transport. Water Resources Research.

Bulliner, E., 2011. Quantifying riparian canopy energy attenuation and stream temperature using an energy balance approach, In *Forestry*. University of Missouri: Columbia, Missouri.

Burt, T., G. Pinay, and S. Sabater (2010), What do we still need to know about the ecohydrology of riparian zones?, Ecohydrology, 3(3), 373-377.

Cardenas, M.B., and Gooseff, M.N., 2008. Comparison of hyporheic exchange under covered and uncovered channels based on linked surface and groundwater flow simulations. Water Resources Research.

Cirmo, C. P., and Mc Donnell, J.J., 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: A review. Journal of Hydrology.

Critchfield, H. J., 1966. General climatology. Prentice-Hall, Englewood Cliffs, New Jersey.

Dahm, C. N., Grimm, N.B., Marmonier, P., Valett, H.M., and Vervier, P., 1998. Nutrient dynamics at the interface between surface waters and groundwaters, Journal of Freshwater Biology., 40, 427-451, doi: 10.1046/j.1365-2427.1998.00367.

Darcy, H., 1856. Principles to follow and formulas to be used in the question of the distribution of water. Public foundations of the city of Dijon.

Duff, J.H., and Triska, F.J., 2000. Streams and Ground Waters. Elsevier Publishing Co., San Diego, California.

Findlay, S., 1995. Importance of surface-subsurface exchange in stream ecosystems: The hyporheic zone. Limnology and Oceanography.

Gilliam J.W., 1994. Riparian wetlands and water quality. Journal of Environmental Quality.

HACH., 2007. DR 2800 Spectrophotometer Procedures Manual, HACH companies.

Harbaugh, A.W. and McDonald, M.G., 1996a. User's documentation for MODFLOW–96, an update to the U.S. Geological Survey modular finite-difference ground-water flow model: U.S. Geological Survey Open-File Report 96 – 485.

Harbaugh, A.W. and McDonald, M.G., 1996b. Programmer's documentation for MODFLOW–96, an update to the U.S. Geological Survey modular finite-difference ground-water flow model: U.S. Geological Survey Open-File Report 96 – 486.

Harbaugh, W. A., Banta., Edward., R., Hill, A.R., Mary, C., McDonald, M.G., Michael, G., 2000. MODFLOW – 2000, The U.S. Geological Survey Modular Ground-Water Model – user guide to modularization concepts and the ground-water flow process. U.S. Geological Survey: Open file report 00 – 92.

Harvey, J.W., and Wagner B.J., 2000. Interactions between Streams and their subsurface Hyporheic Zone. Streams and Ground Waters. Elsevier Publishing Co., San Diego, California.

Hendricks, S. P., and White, D. S., 2000. Stream and groundwater influences on Phosphorus Biogeochemistry. Streams and Ground Waters. Elsevier Publishing Co., San Diego, California.

Hill, A.R., 2000. Stream Chemistry and Riparian Zones. Streams and Groundwater. Elsevier Publishing Co., San Diego, California.

Hurst, C.A., Thorburn, P.J., Lockington, D., and Bristow, K.L., 2004. Sugarcane water use from shallow water tables: implications for improving irrigation water use efficiency, Agricultural Water Management., 65, 1-19. doi: 10.1016/S0378-3774(03)00207-5.

Hynes, H.B.N., 1983. Groundwater and stream ecology. Hydrobiologia.

Jones, J. B., and Mulholland, P. J., 1998. Methane input and evasion in a hardwood forest stream: Effects of subsurface flow from shallow and deep pathways. Limnology and Oceanography.

Jones, J. B., Fisher,S.G., and Grimm,N.B., 1995. Nitrification in the hyporheic zone of a desert stream ecosystem. Journal of the North American Benthological Society.

Jones, J.B., and Mulholland, P.J., 2000.Streams and Ground Waters. Elsevier Publishing Co., San Diego, California.

Kasahara, T., and Wondzell, S.M., 2003. Geomorphic controls on hyporheic exchange flow in mountain streams. Water Resources Research.

Katsyuama, M., Shibata, H., Yoshioka, T., Yoshida, T., Ogawa, A., and Ohte, N., 2009. Applications of a hydro-biogeochemical model and long-term simulations of the effects of logging in forested watersheds. Sustainability Science.

Lautz, L.K., and Siegel, D.I., 2006. Modeling surface and ground water mixing in the hyporheic zone using MODFLOW and MT3D. Advances in Water Resources.

Leopold, A., 1963. Whither Missouri. Dedication address.

Levia, D. F., Carlyle-Moses, D.E., and Tanaka, T., 2011. Reflections on the State of Forest Hydrology and Biogeochemistry, Springer, London, 729-733.

Lins, H.F., and Slack, J.R., 1999. Streamflow trends in the United States. Geophysical Research letters.

Luo, Y., and Sophocleous, M., 2010. Seasonal groundwater contribution to crop-water use assessed with lysimeter observations and model simulations, Journal of Hydrology., 389, 325-335., doi: 10.1016/j.jhydrol.2010.06.011.

Martí, E., Fisher, G.S., Schade, D.J., and Grimm, B.N., 2000. Flood Frequency and Stream-Riparian Linkages in Arid Lands. Streams and Ground Waters. Elsevier Publishing Co., San Diego, California.

McDonald, M.G., and Harbaugh, A.W., 1988. A modular three-dimensional finite difference ground-water flow model. Reston, VA: US Geological Survey.

Milly, P.C.D., Dunne, K.A., and Vecchia, A.V., 2005. Global pattern of trends in streamflow and water availability in a changing climate. Nature.

Moore, I.D.,Turner, A.K.,Wilson, J.P., Jenson, S.K., and Band, L.E., 1993.GIS and land surface–subsurface process modeling. Environmental modeling with GIS. Oxford Univ. Press, New York.

Mulholland, P.J., and Webster, J.R., 2010. Nutrient dynamics in streams and the role of J-NABS. Journal of the North American Benthological Society.

National Research Council (NRC)., 1999. New Strategies for America's Watersheds. National Academy Press. Washington, District of Columbia.

Packman, A.I., and Bencala, K.E., 2000. Modeling surface-subsurface Hydrological interactions. Streams and Ground Waters. Elsevier Publishing Co., San Diego, California.

Pallardy, S.G., Nigh, T.A., and Garrett, H.E., 1988.Changes in forest composition in central Missouri: 1968–1982. American Midland Naturalist.

Poff, N.L., and Ward, J.V., 1989. Implications of Streamflow variability and predictability for Lotic community structure: A Regional analysis of streamflow patterns. Canadian Journal of Aquatic Science.

Ramos, T., Šimůnek, J., Gonçalves, M., Martins, J., Prazeres, A., Castanheira, N., and Pereira, L., 2011. Field evaluation of a multicomponent solute transport model in soils irrigated with saline waters, Journal of Hydrology., doi: 10.1016/j.jhydrol.2011.07.016.

Richards, L. A., 1931. Capillary conduction of liquids through porous mediums, Physics., 1, 318-333.

Rochow, J.J., 1972. A Vegetational Description of a Mid-Missouri Forest Using Gradient Analysis Techniques , American Midland Naturalist.

Šimůnek, J., and Šejna, M., 1999. The HYDRUS-2D software package for simulating the two-dimensional movement of water, heat and multiple solutes in variably-saturated media. Version 2.0, IGWMC - TPS - 53, International Ground water Modeling Center, Colorado School of Mines, Golden, Colorado, 251.

Šimůnek, J., Šejna, M., Saito, H., Sakai, M., and van Genuchten, M.T., 2008. The HYDRUS-1D Software Package for Simulating the Movement of Water, Heat, and Multiple Solutes in Variably-saturated Media. Version 4.0. HYDRUS Software Series 3, Department of Environmental Sciences, University of California Riverside, Riverside, CA, USA. 315.

Šimůnek, J., Wendroth, O., and Van Genuchten, M.T., 1998. Parameter estimation analysis of the evaporation method for determining soil hydraulic properties. Journal of the Soil Science Society of America., 62, 894-905.

Sophocleous, M., 2002. Interactions between groundwater and surface water: the state of the science, Hydrogeolgy Journal., 10, 52-67, doi: 10.1007/s10040-001-0170-8.

Stanley, E.H., and Jones, J.B., 2000. Surface-Subsurface Interactions: Past, Present, and Future. Streams and Ground Waters. Elsevier Publishing Co., San Diego, California.

Storey, R.G., Howard, K.W.F., and Dudley, W.D., 2003. Factors controlling riffle scale hyporheic exchange flows and their seasonal changes in a gaining stream; a three-dimensional groundwater flow model. Water Resources Research.

Strahler, A., 1952. Hypsometric (area-altitude) analysis of erosional topography, Bulletin of the Geological Society of America., 63, 1117-1142.

Triska, F.T., Kennedy, V.C., Avanzino, R.J., Zellweger, G.W., and Bencala, K.E., 1989. Retention and transport of nutrients in a third-order stream in northwestern California: Hyporheic processes: Ecology.

US Department of Agriculture (USDA), N. R. C. S., 2009. Web Soil Survey.

Winter, T.C., Harvey, J.W., Franke, O.L., and Alley, W.M., 1998. Ground water and surface water a single resource: U.S. Geological Survey Circular 1139.

Wondzel, S.M., LaNier, J., Haggerty, R., Woodsmith, R.D., and Edwards, R.T., 2009. Changes in hyporheic exchange flow following experimental wood removal in a small, low-gradient stream. Water Resources Research.

Wood, P.J., Hannah, D.M., Sadler, J.P., 2007. Hydroecology and Ecohydrology: Past, Present and Future. John Wiley and Sons.

Wroblicky, G.J., Campana, M.E., Valett, H.M., and Dahm, C.N., 1998. Seasonal variation in surface-subsurface water exchange and lateral hyporheic area of two stream- aquifier systems. Water Resources Research.

Young, F. J., Radatz, C.A., and Marshall, A., 2003. Soil Survey of Boone County, Missouri Natural Resources Conservation Service, 25 – 35.

CHAPTER II: MEASURING AND MODELING SHALLOW GROUNDWATER AND FLOW CONNECTIVITY TO A FORESTED OZARK BORDER STREAM

2.0. Abstract

Quantitative information is limited pertaining to stream -shallow groundwater interactions in forested riparian zones, in particular karst ecosystems. Spatiotemporal variability of shallow groundwater flow was monitored along two stream reaches in a riparian Ozark border forest of central Missouri using a total of twelve piezometers and four stream-gauging networks during the 2011 water year (WY). High-resolution (i.e. five minute) data showed average groundwater flux of -3 x 10^{-5} m^3 s^{-1} m^{-1} (losing stream) for the entire study reach (total reach length = 830 m) during the 2011 WY. Results indicate rapid groundwater response to rainfall events within 2 to 24 hours as much as nine meters from the stream. Data analyses indicated stream flow loss of 28 and 7% to groundwater during winter and spring, respectively. During the dry season, the stream was gaining 95% of the time. During the wet season, the stream was losing 70% of the time. Based on established assessment criteria, shallow groundwater modeling

performance with HYDRUS – 1D was deemed '*Very good*' (NS = 0.95, r^2 = 0.99, RMSE = 2.38 cm and MD =1.3 cm). Results supply critical baseline information necessary for improved riparian forest management and shallow groundwater biogeochemical transport (e.g. nutrient flux) and storage process understanding in karst ecosystems. Results will assist in development and validation of management tools that contribute to advancements of watershed best management practices in the Ozark border region of the central United States and elsewhere.

2.1. Introduction

Quantifying shallow groundwater flow regime (quantity and timing) is important for effective riparian ecosystem management (Sophocleous, 2002), but is often ignored due to lack of available information. The volume and velocity of shallow groundwater flux can be determined using various methods including Darcy-groundwater flow calculations (McDonald and Harbaugh, 1988) and tracer tests (Jones and Mulholland, 2000a) that quantify the transport of an introduced solute [e.g. sodium chloride, sodium bromide and potassium bromide (Jones and Mulholland, 2000a)]. Other methods include naturally occurring environmental tracers such as water temperature or specific conductivity, and direct measurements of groundwater exchange using devices such as seepage meters (USGS, 2009; 1982). Harvey and Bencala (1993) used numerical models to show groundwater flux of 1.6 x 10^{-6} m^{-3} s^{-1} m^{-1} at St. Kevin Gulch in Colorado, demonstrating stream-groundwater exchange processes influenced by streambed and stream slope variability. Castro and Hornberger (1991) utilized solute tracers in North Fork Dry Run, Virginia, to show that 47% of total catchment water yield was shallow groundwater. Mulholland *et al*. (1997) used seepage meters to show that groundwater flow towards the stream was 2.2 x 10^{-4} m^3 s^{-1} at Walker Branch Creek in North Carolina.

While many methods to estimate shallow groundwater exist, a great deal of research is needed to improve the understanding of groundwater regimes. Dahm *et al*. (1998) concluded that spatiotemporal variations in stream-groundwater exchange processes require investigation in varying geological settings to advance predictive modeling. Sophocleous (2002) emphasized the need for a comprehensive hydrogeoecological framework to better-understand groundwater exchange in relation to land use, geology and biotic factors.

To quantify groundwater flow, many studies utilize a Darcian approach (Darcy, 1856) utilizing an estimated saturated hydraulic conductivity (McDonald and Harbaugh, 1988; Levia *et al*., 2011; Jones and Mulholland, 2000a). Advanced groundwater models, such as HYDRUS – 1D, use variably saturated hydraulic conductivity (Richards, 1931) and can thus simulate both saturated and unsaturated groundwater flow (Bates *et al*. 2000; Dages *et al*. 2008; Šimůnek *et al*. 1998, 1999, 2008; Ramos *et al*. 2011; Ocampo *et al*. 2007; Luo and Sophocleous, 2010). Freely available HYRDUS – 1D has been shown to effectively quantify stream-riparian zone hydrologic connectivity. Luo and Sophocleous (2010) used HYDRUS-1D to estimate groundwater flow values ranging from -3.5 x 10^{-8} to 3.5 x 10^{-8} m s^{-1} with a coefficient of determination (r^2) value of 0.75 between simulated and measured groundwater flow in an agricultural field located in Shandong province, China.

A number of numerical groundwater models (e.g. CPFLOW, MODFLOW, SUTRA, HYDRUS and FEFLOW) (Maest and Kuipers, 2005) have been shown to successfully predict vertical surface – subsurface interactions. However, previous authors indicated that improved model accuracy requires proper parameterization, emphasizing the need for higher resolution (spatial and temporal) field observations (Hurst *et al*. 2004; Katsuyama *et al*. 2009). Shallow groundwater flow studies that integrate in-situ field and modeling methodologies are necessary to improve quantitative understanding and consequently management of groundwater resources (Abesser *et al*. 2008; Dahm *et al*. 1998; Akerman and Stein, 2008; Sophocleous, 2002).

While studies are geographically dispersed, the majority of previous studies were conducted in the North-Western United States, (Tabacchi *et al*. 2000; Castro and Hornberger, 1991; Valett *et al*. 1990) or outside the United States (Burt *et al*. 1999; 2002a; 2002b; Bosch, 1979; Abesser *et al*. 2008). Castro and Hornberger (1991) used tracers to quantify surface-subsurface water interactions in North Fork Dry Run, Shenandoah National Park, Virginia, quantitatively characterizing the connectivity of surface-subsurface water and nutrient flow. Volume flow estimates were compared with results from physically based nutrient transport models. The authors showed that physically based models need to account for interactions between the stream and the floodplain to effectively model transport and storage of water in riparian zones. They concluded that it is necessary to include water table variations in the riparian zone for numerical modeling approaches. Burt *et al*. (2002a, 2002b) replicated experimental designs in France, the Netherlands, Poland, Romania, Spain, Switzerland and the United Kingdom by constructing dipwell grids at each site to map water table levels in the riparian zone, including riparian woodland and upslope areas. Their study results characterized riparian water table influence by adjacent receiving water bodies. The observed variations in riparian zone hydraulic gradients and water table level and flow patterns were attributed to surface water –groundwater interactions along with runoff (surface and subsurface) from surrounding hills. Their results showed a net increase in ground water level 40 m away from the stream, at the French (50 cm), UK (150 cm), Romanian (0.6 cm), Spanish (200 cm), Dutch (300 cm) and Polish (150 cm) sites during 2009, collectively indicating greater upslope contributions to riparian groundwater relative to localized surface water –groundwater interactions. Despite breakthroughs such as these in other regions, there remains a critical need for shallow groundwater research in the central United States where there are marked differences in riparian forest species, hydrogeology and climate.

The objectives of this following study were to a) quantify spatial and temporal variability of shallow groundwater and stream water exchange in a karst ecosystem of the central U.S over the period of one water year, b) validate the groundwater flow model HYDRUS – 1D, c) by virtue of the first two objectives, improve model predictive confidence in karst hydro-systems of the central U.S; and d) advance shallow groundwater and stream water process understanding and therefore management of hydrologically distinct central U.S. and Ozark border riparian forests.

2.2. Study site

This study took place on two reaches of Brushy Creek located within the Thomas S. Baskett Wildlife Research and Education Area (BREA) (Figure 2.1.). The BREA is located at UTM15 coordinates 569517 E and 4289338 N, 8 km east of Ashland, in the Ozark border region of South-central Missouri, U.S. (Pallardy *et al*. 1988). Brushy Creek is a second order stream (Strahler, 1952) with average slope of 0.94%, joining Cedar creek 4 km south of the BREA, after draining a watershed of approximately 9.17 km^2. Current land use ranges from second growth forests to pastures. The watershed consists of 2.6% suburban land use, 17.9% cropland, 33% grassland, 43.2% forest, and 3.3% open water and wetlands (USDA, 2009).

Limestone geology of Ordovician and Mississippian age underlies the BREA. Dominant soils are Weller silt loam and Clinkenbeard clay loam (Rochow, 1972). Streambed sediments, primarily composed of coarse gravel, cobble and cherty fossilized materials, are less than one-meter deep, overlying bedrock and layered limestone (Keller, 1961). Soil within the riparian zone (RZ) consists of a mix of Cedargap and Dameron soil complexes (USDA soil map unit 66017). BREA soils have average bulk density of 1.2 to 1.4 g cm^{-3}. Soils are well-drained and are frequently flooded soils of alluvial parent material (Young *et al*. 2001). Vegetation consists of northern and southern division oak-hickory forest species (Rochow, 1972) including American Sycamore (Platanus occidentalisi), American Elm (Ulmus americana) and Black Maple (Acer nigrum) dominated riparian reaches (Belden and Pallardy, 2009). Understory vegetation is dominated by sugar maple (Acer saccharum), flowering dogwood (Cornus florida), and black cherry (Prunus serotina) (Reed, 2010).

Climate in the BREA is classified as humid - continental (Critchfield, 1966). Mean January and July temperatures are -2.2 °C and 25.4 °C (1971-2010), respectively, while mean annual precipitation is 1037 mm, as recorded at the Columbia Regional Airport located 8km to the north of the BREA (Belden and Pallardy, 2009).

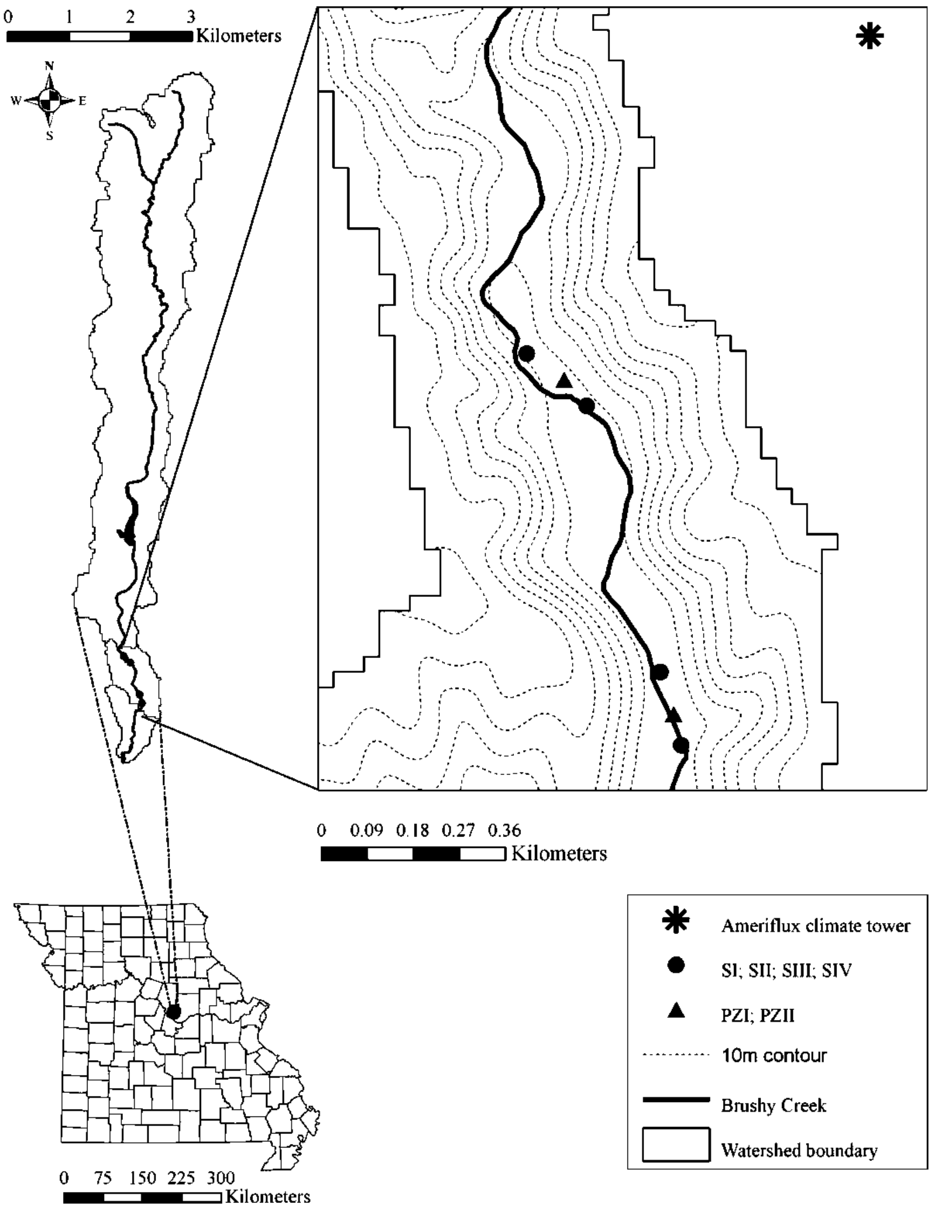

Figure 2.1. Study sites and instrument locations at Baskett Wildlife Research and Education Area, central Missouri, U.S. S = stilling well sites. PZ = piezometer sites.

2.3. Methods

2.3.1. Instrumentation and data collection

Climate data were obtained from an AmeriFlux tower (Gu *et al*. 2007) installed at an elevation of 238 m (Figure 2.1.), and obtained via a public ftp server: (ftp://ftp.atdd.noaa.gov/pub/GEWEX/2010/mo/). Stream stage monitoring sites (hereafter referred to as SI – SIV, n=4) were installed before and after each piezometer array (Figure 2.1.). The distance from SI-SIV was 830 m, while distance between SI-SII, SII-SIII, SI-SIII and SIII-SIV were 160, 543, 682 and 149 m, respectively. Stilling wells were equipped with Solinst® Levelogger Gold pressure transducers (error ±0.003 m) and programmed to record stream stage at five minute intervals. To obtain high spatial resolution information, shallow groundwater levels were monitored using piezometers installed in the RZ up to 9 m perpendicular from the stream bank (Figures 2.1. and 2.2.). Between site one (SI) and site two (SII), four piezometers (Pz1, Pz2, Pz3 and Pz4) were installed in a transect (Piezometer Site I, hereafter referred to as PZI) extending from 3 m from the stream edge to 9 m in to the RZ (Figure 2.2.). Piezometer Site II (PZII) was located 660 m S-SE of PZI with four piezometers (Pz5, Pz6, Pz7 and Pz8). Each 3.6 m long drive-point piezometer with 4 cm inner diameter and 76 cm slotted screen at the end was equipped with Solinst® Levelogger Gold programmed to log water depth at five minute intervals.

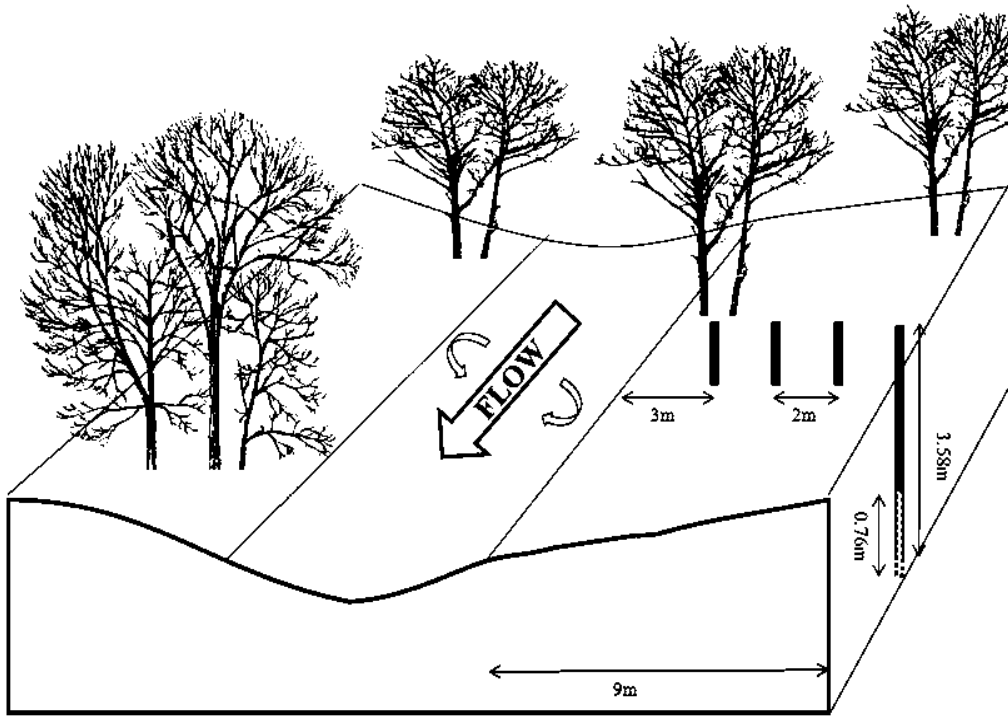

Figure 2.2. Conceptual diagram of cross-section of piezometer study design at Baskett Wildlife Research and Education Area, central Missouri, U.S. Elevation of each well was measured independently and head measurements were normalized to elevation common to both piezometer sites PZI and PZII.

2.3.2. Quantifying stream flow

Streamflow rating curves for each stage monitoring site were developed using measured stage-discharge relationships established by the stream cross section method (Dottori *et al*. 2009) using a Marsh-McBirney ® Flo-Mate flow meter (sensor error ± 2%). Stream cross section flow measurement campaigns were performed by the same personnel and for various flow depths to minimize computational errors (Baraca, 2008; USGS, 1982). Rating curves were calculated as per Dottori *et al*. (2009):

$$Q = a \times Z^b \qquad [1]$$

where Q is discharge in units of volume per unit time, Z is measured stream stage in units of length, and a and b are coefficients determined by stream morphology.

2.3.3. Quantifying shallow groundwater flow

Shallow groundwater flow was calculated using Darcy's Law (1856):

$$Q_s = K_s \times \nabla h \times A \qquad [2]$$

where Q_s is shallow groundwater flow ($m^3\ s^{-1}$), K_s is hydraulic conductivity ($m\ s^{-1}$), ∇h is the hydraulic gradient ($m\ m^{-1}$), where $\nabla h = \Delta h/\Delta l$ where Δh = change in head change between piezometers (m), Δl is the flowpath length between piezometers (m) and A is the cross section area (m^2). Saturated hydraulic conductivity (K_s), estimated using the piezometer method (standard slug test) (Amoozegar, 2002), was $3 \times 10^{-5}\ m\ s^{-1}$ at PZI and $1 \times 10^{-5}\ m\ s^{-1}$ at PZII. Estimated K_s values corresponded to silty sand deposits (Freeze and Cherry, 1979) and agreed with results from BREA provided by Rochow (1972). The shallow groundwater cross section area (A) was computed as the average wetted thickness using the average depth in the piezometer and the distance between piezometers. Since the depth to the bedrock was within a maximum of three meters, the shallow groundwater zone was assumed primarily of alluvial composition (see Study Site), and barring other information, a homogeneous soil matrix with a corresponding representative K_s value was assumed.

Darcy velocity (*v*) for the shallow groundwater flow was calculated as per *Darcy* (1856) and as used in Sophocleous (2002), Ocampo *et al*. (2006) and Wondzell (2011):

$$v = \frac{Q_s}{A}$$ [3]

Darcy velocities along the piezometer transect were approximately 4.7 x 10^{-5} and 1.1 x 10^{-6} cm s^{-1}at PZI and II, respectively. Average linear velocity of shallow groundwater flow was estimated as per Freeze and Cherry (1979) and as used in Levia *et al*. (2011) and Jones and Mulholland (2000):

$$\vec{v} = \frac{Q}{nA}$$ [4]

where $\vec{v}$ is the average linear velocity and *n* is the effective porosity. Based on porosity data summarized by Davis (1969) for various geologic materials, silty sand was assumed to have an effective porosity of 0.35 to 0.50.

2.3.4. Quantifying groundwater flux

Assuming equivalent precipitation and evapotranspiration processes along the study reaches, the groundwater flux was estimated using the mass balance approach:

$$\frac{dQ}{dx} = Q_h$$ [5]

where Q_h is the net groundwater flux ($m^3 s^{-1} m^{-1}$), dQ is the difference in stream flow ($m^3 s^{-1}$) measured at the upstream and downstream sampling locations of the piezometer transect and dx is the distance (m) between stilling wells (Harvey and Bencala, 1993; Harvey and Wagner, 2000a, 2000b; Scordo and Moore, 2009).

2.3.5. Numerical simulation with HYDRUS – 1D model

HYDRUS – 1D characterizes infiltration, evaporation, transpiration, percolation, water flow, solute flow and heat flow through variably-saturated (vadose and saturated zone) porous soil media (Radcliffe and Šimůnek, 2010; Šimůnek *et al*. 2002, 2008, 2009; Ramos *et al*. 2011). The model focuses on lateral movement of groundwater within confined boundary conditions and thus requires less computing power and time relative to 2D or 3D simulations, and is therefore considered a relatively user friendly management tool (Dages *et al*. 2008). Given its relative ease of use, and applicability for the current work, the conceptual model representing the RZ was calibrated and validated with HYDRUS – 1D using measured groundwater head data from the piezometers located in PZI and II as per the methods of Dages *et al*. (2008).

2.3.5.1. HYDRUS – 1D computations

In HYDRUS – 1D, groundwater flow is quantified using Richards's equation (Richards, 1931):

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x}\left\{K(h)\left(\frac{\partial h}{\partial x} - cos \propto\right)\right\} - S(x,t) \qquad [6]$$

where θ is volumetric soil water content ($m^3\ m^{-3}$), t is time (s), x is the horizontal space coordinate (m) (for lateral flow), h is pressure head (m), S is the water sink term ($m^3\ m^{-3}\ s^{-1}$), α is the angle between the flow direction and the vertical axis (i.e. $\alpha = 0°$ for vertical flow, 90° for horizontal lateral flow, and $0° < \alpha < 90°$ for inclined flow) and K is unsaturated soil hydraulic conductivity ($m\ s^{-1}$) given by:

$$K(h,x) = K_s(x)\ K_r(h,x) \qquad [7]$$

where K_r is relative hydraulic conductivity (unitless) and K_s is saturated hydraulic conductivity ($m\ s^{-1}$). The soil hydraulic properties and water retention parameters used in the model for the current study, θ_r – residual soil water content ($m^3\ m^{-3}$), θ_s – saturated soil water content ($m^3\ m^{-3}$), α –parameter α in the soil water retention function (m^{-1}), n - parameter n in the soil water retention function (unitless), K_s - ($m\ s^{-1}$), l - tortuosity (unitless), are described using a set of closed form equations developed from van Genuchten–Mualem functional relationships (van Genuchten, 1980). K_r is a function of hydraulic head (h) and distance (x). Van Genuchten (1980) defined the normalized water content (Θ) to explain K_r, where Θ is also called effective saturation. The θ_r can be defined as the water content for which the ratio of the change in volumetric content to the change in hydraulic head becomes zero (van Genuchten, 1980). The θ_s is mostly assumed to be the same as the soil porosity (Hillel, 2000). In addition, HYDRUS - 1D uses a

Marquardt Levenberg type soil parameter estimation technique for inverse estimation of soil hydraulic parameters from measured hydraulic head data (h) (Šimůnek *et al*. 2009). A detailed description of parameter optimization and statistics of the inverse solution is provided in Šimůnek *et al*. (2009).

2.3.5.2. HYDRUS – 1D data forcing

Observed RZ groundwater head values served as initial conditions for the simulation. Due to the availability of high frequency data, upper and lower boundary conditions were set as a variable pressure head type in HYDRUS – 1D. Accordingly, observed hydraulic head values from the piezometers closest (Pz1 at site PZI and Pz5 at site PZII) and furthest (Pz4 at site PZI and Pz8 at site PZII) from the stream served as time dependent boundary values for the finite grid element created in HYDRUS - 1D. The observed RZ groundwater head from the remaining two piezometers at each site (Pz2, Pz3 and Pz6, Pz7 at site PZI and PZII, respectively) was used for model validation. The governing flow equation (Equation 6) was solved numerically using a standard Galerkin-type linear finite element scheme (Šimůnek *et al*. 2009).

Initial soil hydraulic parameters were estimated using pedotransfer functions (PTFs), by supplying textural class and two groundwater head values as input data (Schaap *et al*. 1998) to ROSETTA, a built-in computer program in HYDRUS – 1D (Schaap *et al*. 2001). For initial estimation of soil properties, soil texture classes were identified as silt loam based on the results of previous work in the BREA (Pallardy *et al* 1988; Krusekopf and Scrivner, 1962; Garrett and Cox, 1973). A 6 m horizontal soil cross-section was defined for each piezometer site. Four nodes, fixed along the soil cross section, represented each piezometer location. The initial soil water content (θ_s) was set to a uniform value of 0.43 $m^3 m^{-3}$ (using PTFs for silt loam). Measured groundwater head values, at each node were simulated in HYDRUS – 1D to obtain soil hydraulic parameters using the inverse solution method (Luo and Sophocleous, 2010; Šimůnek *et al*. 1998; Dages *et al*. 2008; Yu *et al*. 2009; Šimůnek *et al*. 2005). The final set of soil hydraulic parameters with the best coefficient of determination (r^2) relationship between observed and modeled hydraulic head values was used to model groundwater flow.

2.3.5.3. HYDRUS – 1D calibration, validation and statistical analysis

HYDRUS – 1D was calibrated for a three-month period (April 2010 to June 2010). Final soil hydraulic parameters obtained from calibration were then used for validating the model for a three-month period (July 2010 to September 2010). To quantify model bias, simulated and observed hydraulic head values were evaluated using the Nash-Sutcliffe Efficiency parameter (NS) (Nash and Sutcliffe, 1970), the Root Mean Square Error (RMSE) (Willmott, 1981), the Mean Difference (MD) (as used by Swain *et al*. 2004) and the standard regression method. Model outputs were rated '*Very Good*', '*Good*', '*Satisfactory*', or '*Unsatisfactory*' according to the criteria recommended by Moriasi *et al*. (2007). The Nash-Sutcliffe (NS) efficiency parameter was used to evaluate how well HYDRUS – 1D predicted observed hydraulic head variability relative to the average observed value for the selected time period (Equation 8). The NS parameter value ranges from $-\infty$ to 1.0 where 1.0 indicates the model is in perfect agreement with the observations and < 0.0 when there is a poor agreement (Moriasi *et al*. 2007; Luo and

Sophocleous, 2010). RMSE values closer to zero indicate better model performance (Moriasi *et al*. 2007). Assuming that observed and simulated values are linearly related, the equation of the best-fit regression line (coefficient of determination) can indicate how well modeled values agree with observed values (Luo and Sophocleous, 2010). Further information regarding the indices NS, RMSE, MD and standard regression is presented in Moriasi *et al*. (2007). The equations to calculate the aforementioned statistics are as follows:

$$NS = \frac{voN - \sum_{i=1}^{N}(x_i - yi)^2}{voN} = 1 - \frac{\sum_{i=1}^{N}(x_i - yi)^2}{\sum_{i=1}^{N}(x_i - \bar{x})^2} \qquad [8]$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(x_i - yi)^2}{N}} \qquad [9]$$

$$MD = \frac{1}{N}\sum_{i=1}^{N}(x_i - yi)^2 \qquad [10]$$

where *vo* is the variance of observed values, N is the number of data points, *xi* is the observed value, *yi* is the corresponding predicted value and $\bar{x}$ is the average observed value for the study period.

2.4. Results and Discussion

2.4.1. Hydroclimate during study

Climate at the BREA during WY 2011 was characteristically variable with mean air temperature of 12.5 ˚C and total precipitation of 647 mm. It was on average cooler and drier during the study relative to average temperature and precipitation (13˚C and 930 mm, respectively) recorded at the Ameriflux tower between 2005-2010. Seasonal precipitation during WY 2011 (winter, spring, summer, fall) was 170 mm (December - March), 250 mm (March – June), 135 mm (June – September) and 94 mm (September to December). Stream flow was ephemeral, exhibiting high flows in spring and summer, and drying by mid-October. Error associated with streamflow measurements and stream stage errors was estimated to be ±1.05 x 10^{-4} m^3 s^{-1} and therefore assumed negligible.

Carter (1963) estimated that flow meter velocity observation error, measured at 45-second intervals, at 0.2, 0.6 and 0.8 depths was less than 2.3%. Annual stream flow at SII was 44% greater than streamflow at SI, indicating that the stream reach (between SI and SII) was, on average, a gaining stream (Figure 2.3. and Table 2.1.). Figure 2.3. shows temporal trends in stream stage and depth to groundwater. Average stream flow at SIV was twice that of SIII (with 218% increase in stream flow), indicating that the stream reach (between SIII and SIV) was also gaining. There was negligible surface flow from October 15 to November 23, 2010 (27 mm of precipitation), during which time stream-shallow groundwater flow could not be quantified using Equation 5 (Figures 2.4. and 2.5.). Average daily stream flow during the study period was 0.22 m^3 s^{-1} at SII followed by SI (0.16 m^3 s^{-1}), SIV (0.13 m^3 s^{-1}) and SIII (0.04 m^3 s^{-1}), indicating that the stream was intermittently gaining and losing along the entire reach.

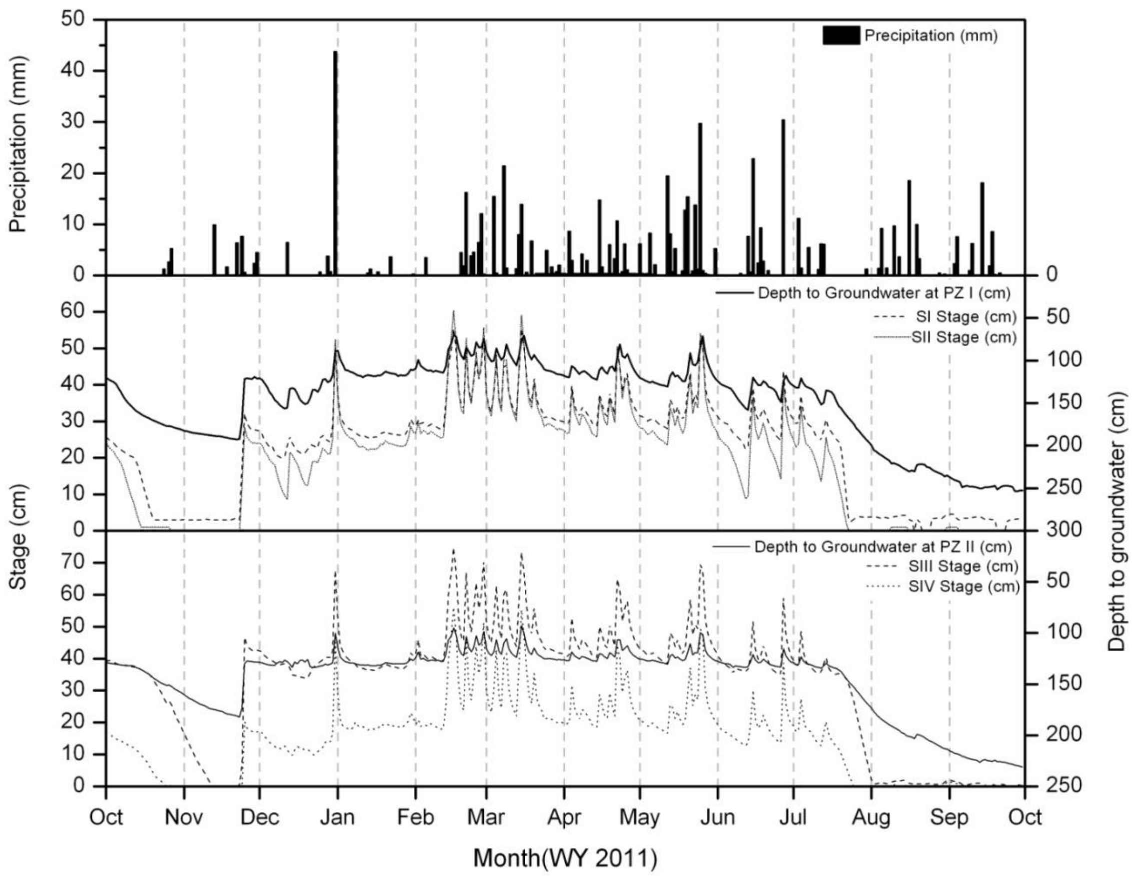

Figure 2.3. Measured rainfall (mm), stream stage (cm) and average depth to groundwater (cm) at piezometer sites during WY 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

Table 2.1. Stream discharge (m^3 s^{-1}) descriptive statistics for WY 2011 of Brushy Creek flow monitoring sites at Baskett Wildlife Research and Education Area, central Missouri, U.S.

Site	SI (m^3 s^{-1})	SII (m^3 s^{-1})	SIII (m^3 s^{-1})	SIV (m^3 s^{-1})
Mean	0.16	0.22	0.04	0.13
Std. Deviation	0.45	0.29	0.13	0.23
Minimum	0.00	0.00	0.00	0.00
Maximum	3.80	1.78	1.22	1.59

2.4.2. Groundwater flux

High-resolution (i.e. five minute) stream stage and groundwater level data showed that average annual groundwater flux was -3 x 10^{-5} m^3 s^{-1} m^{-1} (thus losing stream) for the entire study reach (SI to SIV, total reach length = 830 m), and was 4 x 10^{-4} and 6 x 10^{-4} m^3 s^{-1} m^{-1} for the stream reaches SI-SII and SIIII-SIV, respectively (Table 2.2.). Figures 2.4. and 2.5. show groundwater flow relationships between stilling wells SI-SII and SIII-SIV. Flow results are higher (99% difference) than the results of Wroblicky *et al*. (1998) of 8 x 10^{-8} and -1 x 10^{-8} m^3 s^{-1} m^{-1}. The majority of the difference is attributed to lower relative soil hydraulic conductivity (6 x 10^{-8} m s^{-1}) and a 77% smaller watershed area (3.22 km^2) at Aspen Creek, New Mexico. Obviously, karst geology of the BREA may increase groundwater flux values. Direct karst geological influence of results was beyond the scope of the current work, but supplies impetus for future investigations.

In the current work, average groundwater flow towards the stream was 0.07 and 0.09 m^3 s^{-1} at SI-SII and SIII-SIV, respectively. Maximum daily groundwater flow was 0.27 and 0.51 m^3 s^{-1} (gaining stream) while the minimum groundwater flow was -2.07 and -0.001 m^3 s^{-1} (losing stream) at SI-SII and SIII-SIV, respectively. There was therefore an 88% difference of flow between the two distinct study reaches. Estimated groundwater flow of -2.07 $m^3 s^{-1}$ at SI (negative sign indicates losing stream) was consistent with observed decrease in depth to groundwater of 75.32 cm (from 105.79 cm on March 15, 2011) at PZI. Figure 2.3. shows the relationships in this karst system between depth to groundwater and stream stage, illustrating a high degree of shallow groundwater connectivity between the stream and adjacent RZ. Maximum daily groundwater flow (0.51 $m^3 s^{-1}$) coincided with minimum depth to groundwater from the surface of the soil (101.93 cm on February 17, 2011) at PZII. During WY 2011, groundwater flow accounted for approximately 0.07 and 0.09 $m^3 s^{-1}$ of the mean daily stream discharge of 0.22 $m^3 s^{-1}$ for SII and 0.13 $m^3 s^{-1}$ for SIV. However, for the entire length of the study reach, SI to SIV, (830 m), a mean daily discharge of -0.03 $m^3 s^{-1}$ was lost to the aquifer during WY 2011 (Tables 2.2. and 2.3.).

Daily average stream discharge at SIV was 84% higher during winter and spring (0.25 and 0.20 $m^3 s^{-1}$) seasons, compared to fall and summer (0.04 and 0.02 $m^3 s^{-1}$). During the brief period when streamflow was negligible, average groundwater flow towards the stream was two orders of magnitude greater at SIII-SIV (5 x 10^{-4} $m^3 s^{-1}$) relative to SI-SII (7 x 10^{-6} $m^3 s^{-1}$). During the winter season, SIII-SIV had 0.10 $m^3 s^{-1}$ more water flow from the RZ relative to SI-SII. Ultimately, groundwater input to the stream accounted for 27% of the total stream discharge volume at stream reach one (PZI) and 69% at stream reach two (PZII) during WY 2011. This result corroborates the results of previous authors that showed that shallow groundwater flow directions near the stream are highly spatially variable and bidirectional with shallow groundwater flowing intermittently towards and away from the stream (e.g. Wondzell and Swanson, 1996;

Marzolf *et al*. 1994). Marzolf *et al*. (1994) reported average stream flow of 0.003 and 0.002 $m^3 s^{-1}$ during summer and fall seasons (i.e. one-tenth the flow of Brushy Creek, with reach length = 830 m) with groundwater flow of 1×10^{-4} and 2×10^{-4} $m^3 s^{-1}$ (i.e. one-hundredth the groundwater flow observed at SIV-SIII, Brushy creek) in Walker Branch Creek in Tennessee (reach length = 62 m). The higher flow in Brushy Creek relative to the Walker Branch Creek study is explained in part by larger drainage area and study reach length. The groundwater flux at Walker Branch Creek (1×10^{-5} $m^3 s^{-1} m^{-1}$) was 10% that of Brushy Creek (4×10^{-4} $m^3 s^{-1} m^{-1}$), thus proportionally corroborating similar drainage area-stream-groundwater exchange patterns between the two studies.

Table 2.2. Average stream discharge difference (∂Q in $m^3 s^{-1}$) and average groundwater flux rate ($\partial Q/\partial x$ in $m^3 s^{-1} m^{-1}$) at four monitoring sites during water year 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

	Groundwater Flow Between Gauging Sites ($m^3 s^{-1}$)			Groundwater Flow per unit Stream Length Between Gauging Sites ($m^3 s^{-1} m^{-1}$)		
Site	SI	SII	SIII	SI	SII	SIII
SI	-			-		
SII	0.07	-		4.2×10^{-4}	-	
SIII	-0.12	-0.18	-	-1.7×10^{-4}	-3.4×10^{-4}	-
SIV	-0.03	-0.1	0.09	-3.4×10^{-5}	-1.4×10^{-4}	5.8×10^{-4}

Table 2.3. Descriptive statistics of groundwater flow ($m^3 s^{-1}$) between three study site locations at Baskett Wildlife Research and Education Area, central Missouri, U.S.

Descriptive Statistics	Groundwater Flow ($m^3 s^{-1}$)		
	Entire Study Reach SI -SIV	Between SI-SII	Between SIII-SIV
Mean	-0.03	0.07	0.09
Standard Deviation	0.08	0.27	0.51
Minimum	-2.23	-2.07	0.00
Maximum	0.24	0.23	0.11

2.4.3. Shallow groundwater interflow

Average depth to groundwater was 69.70 cm at PZI and 92.32 cm at PZII during spring months (February to June with 32% difference between sites), and 253.41cm at PZI and 231.30 cm at PZII during fall months (September to December with 8% difference between sites) (Figure 2.3. and 2.7.). During the dry season (October – November with 8% difference between sites), depth to groundwater was 214.9 cm and 197.61 cm at PZI and PZII, respectively, and water level in the piezometers dropped below average level (126.62 and 150. 93 cm at PZI and PZII). Generally, when groundwater level fell below average (126.62 and 150. 93 cm at PZI and PZII), groundwater contribution to surface discharge was low and thus a lower stream flow was observed. However, after a series of precipitation events during the last week of December 2011, shallow groundwater recharged and hydraulic head increased to 229.08 and 230.71cm at PZI and PZII. Conversely, under negligible stream flow conditions, there was decreased variability of groundwater level across the RZ at both PZI (< 1%) and PZII (< 1%). Results of hydraulic gradient analysis are provided in Table 2.4. A negative gradient implies groundwater movement towards the stream. The aforementioned variation in the direction of water movement is typical of streams of arid areas or streamflow in dry seasons (Hughes, 1990).

Shallow groundwater flow also depends on a number of additional hydroclimatic factors including, but not limited to, air temperature, evapotranspiration, soil water saturation and unsaturated zone depth (Lewandowski *et al*. 2009; 2007) and evapotranspiration and plant water storage (Lewandowski *et al*. 2009). Both exfiltration and infiltration processes have ecological importance, as the amount of water stored in the RZ and how far surface water infiltrates controls transport of key nutrients such as nitrate, phosphorous and potassium (Burt *et al*. 1999, Jones and Mulholland, 2000a, 2000b; Tabacchi *et al*. 2000; Lewandowski and Nutzmann, 2007).

Table 2.4. Descriptive statistics of hydraulic gradient (cm) for shallow groundwater monitoring sites (PZI and PZII) for water year 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

Site	Hydraulic gradient (cm)	
	PZI	PZII
Mean	-10.05	5.65
Standard Deviation	6.27	3.30
Minimum	-32.47	-5.90
Maximum	0.90	10.21

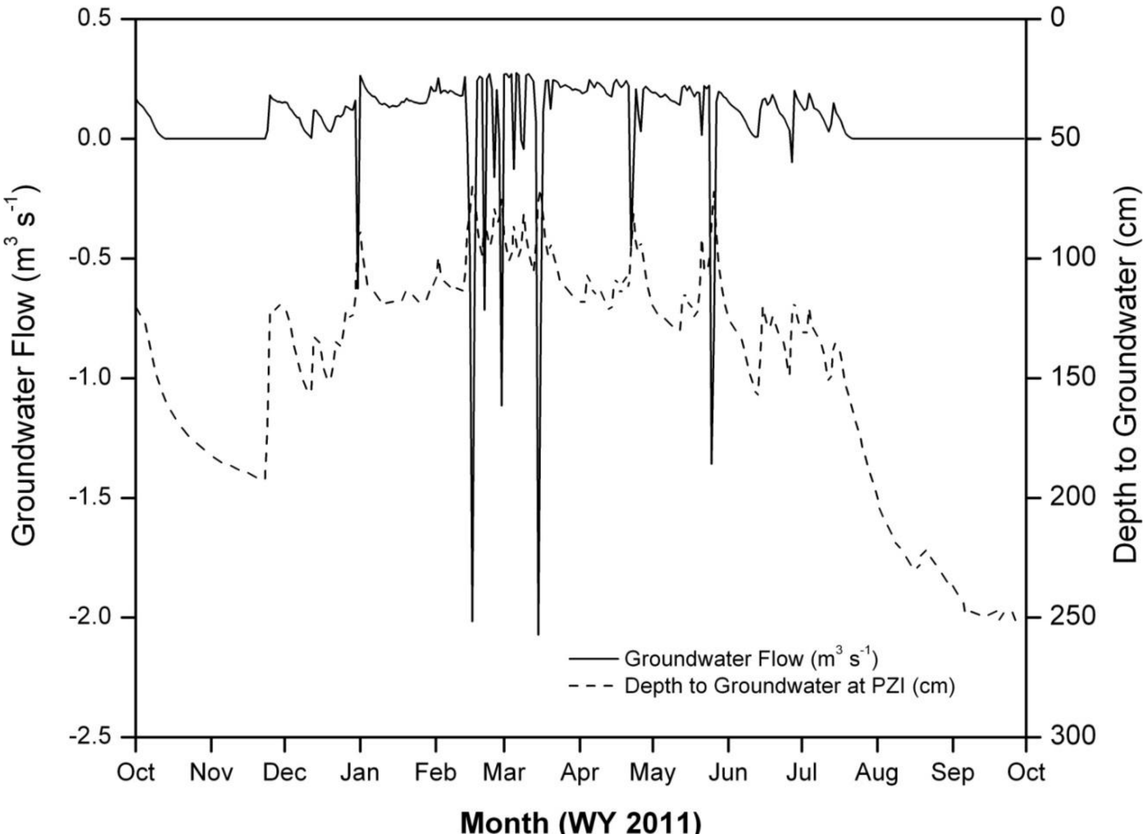

Figure 2.4. Average groundwater flow (m^3 s^{-1}) and depth to groundwater (cm) at SI-SII (PZI), with average of four wells, for water year 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

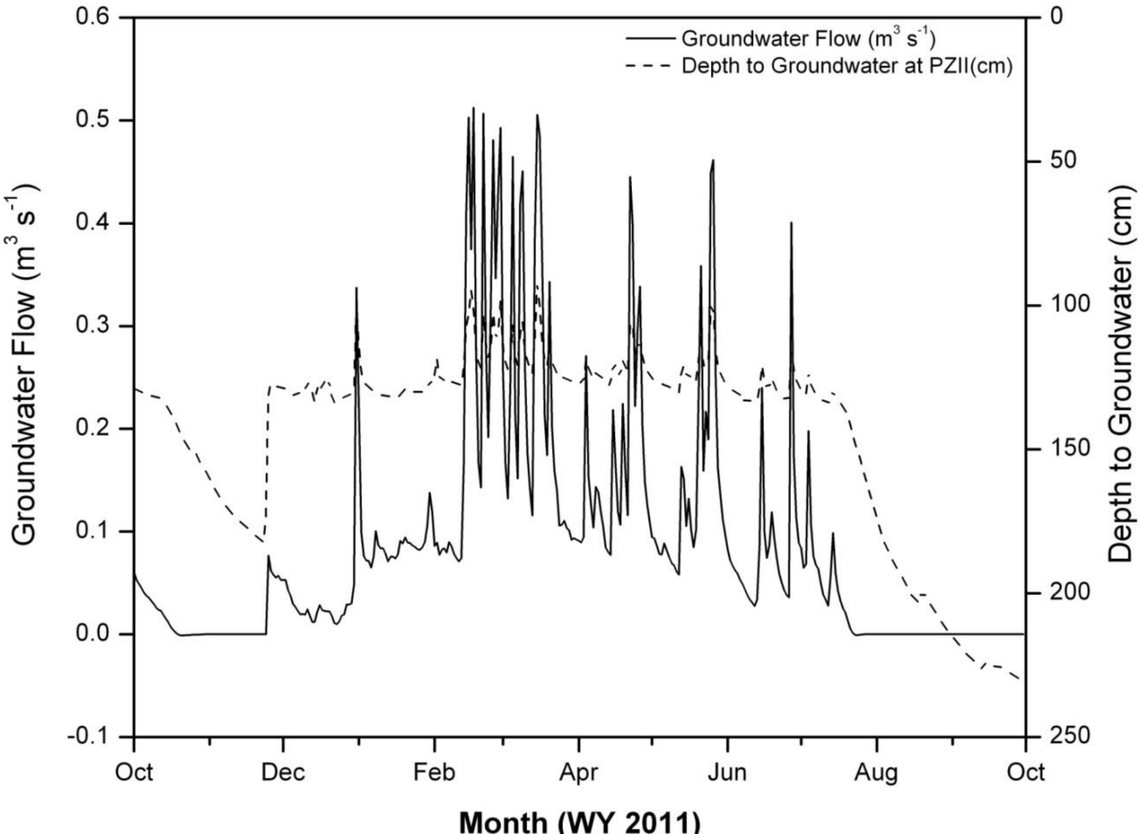

Figure 2.5. Average groundwater flow ($m^3\ s^{-1}$) and depth to groundwater (cm) at SIII-SIV (PZII), (n = 4 wells), for water year 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

2.4.4. Modeling with HYDRUS - 1D

2.4.4.1. Calibration of HYDRUS – 1D

As per calibration outcomes (April to June 2010) the following soil hydraulic parameters were used 0.065 $m^3\ m^{-3}$, 0.41 $m^3\ m^{-3}$, 0.075 m^{-1}, 1.89, $1.\ 2 \times 10^{-5}$ m $s^{-}1$ and 0.5 for θ_r, θ_s, α, n, K_s and l, respectively (see Methods), with r^2 values of 0.98 and 0.90 for PZI and PZII, respectively (Table 2.5.). Simulated hydraulic head values were compared to observed hydraulic head values to validate (July 2010 to September 2010) the model as per the methods of Dages *et al*. (2008). Model calibration resulted in r^2

values of 0.99 and 0.97 at PZI and PZII, respectively. Model calibration Nash-Sutcliffe, RMSE and MD ranged from 0.99 to 0.98, 2.47 to 5.60 cm and -0.86 to 1.49 cm at PZI and PZII respectively.

2.4.4.2. Validation of HYDRUS – 1D

HYDRUS – 1D simulations were run for the 2011 WY for both sites (PZI and PZII) using validated soil hydraulic parameters with r^2 values ranging from 0.99 to 0.98 at PZI and 0.98 to 0.96 at PZII. Model validation Nash-Sutcliffe values ranged from 1.00 to 0.99 at PZI, with the former for the hydraulic head in the piezometer most adjacent to the stream, indicating an excellent fit of the modeled hydraulic head to observed hydraulic head. For PZII, NS values ranged from 0.99 to 0.90, indicating a very good fit of the modeled hydraulic head. The RMSE ranged from 2.38 cm to 3.51 cm, while the MD ranged from 1.30 cm to 2.36 cm between the stream and PZI. For PZII, RMSE ranged from 2.92 cm to 11.16 cm, while the MD ranged from 2.24 cm to 10.08 cm. The coefficient of determination (r^2) between observed and modeled hydraulic head was 0.99 for both PZI and PZII, respectively (Table 2.5.). Model statistics (Table 2.5.) indicated that HYDRUS – 1D, along with the soil hydraulic parameters, was accurate in predicting the hydraulic head measurements at PZI and PZII for the study period and was thus rated '*Very Good*' according to the criteria set by Moriasi *et al*. (2007). HYDRUS - 1D predicted Ks values of 1.2 x 10^{-5} m s^{-1} which is in close agreement with the average Ks measured from field measurements (1.5 x 10^{-5} m s^{-1}) and also in agreement with Ks predicted from USDA - National Resources Conservation Service (NRCS) Web Soil

Survey (WSS) (USDA, 2009) (1.25 x 10^{-5} m s^{-1}). Figure 2.6. compares modeled hydraulic heads against observed heads for the entire study period.

Table 2.5. Model performance statistics comparing observed versus modeled Hydraulic Head (Hp) (cm) between piezometer site PZI and PZII, for the calibration period (April to June 2010) at Baskett Wildlife Research and Education Area, central Missouri, U.S.

Model Node	r^2	NS	RMSE(cm)	MD (cm)
Piezometer		Piezometer site PZI		
Pz2	0.99	0.99	2.38	1.3
Pz3	0.99	0.99	3.51	2.36
		Piezometer site PZII		
Pz6	0.99	0.99	2.92	2.24
Pz7	0.98	0.9	11.16	10.08

NS=Nash-Sutcliffe; RMSE=Root Mean Squared Error; MD=Mean Difference

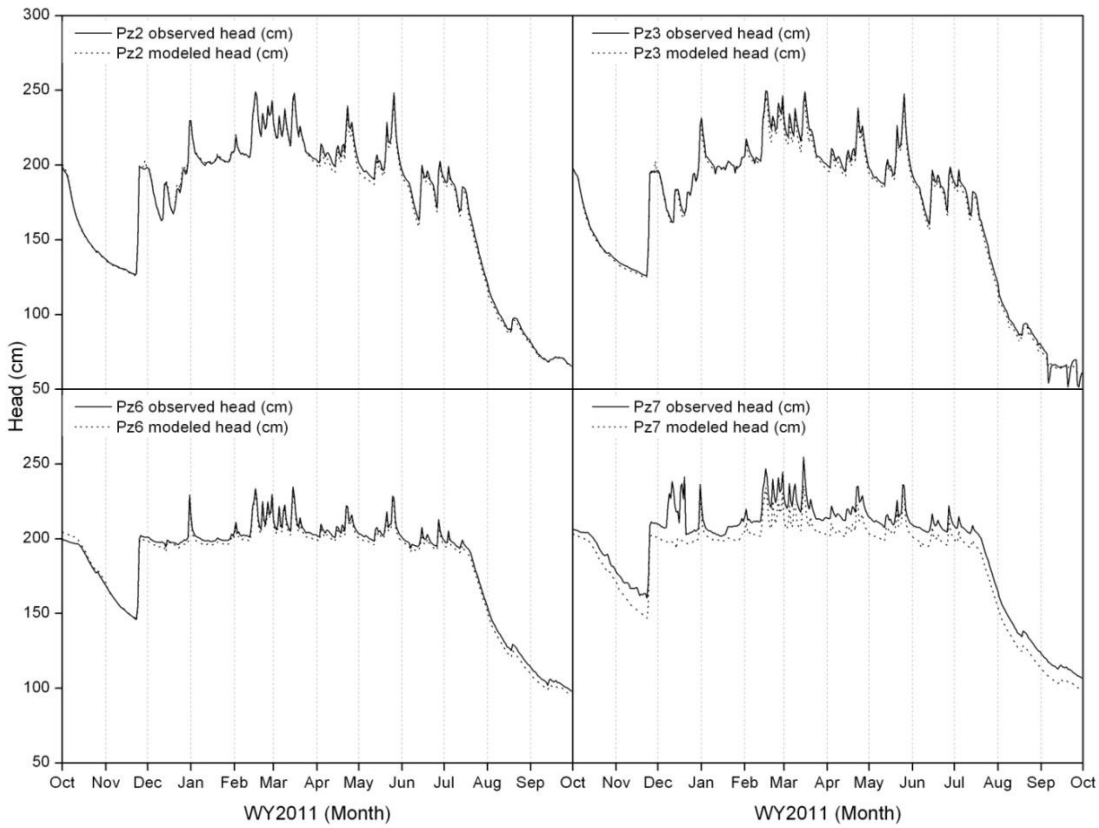

Figure 2.6. Observed versus HYDRUS – 1D modeled hydraulic head (Hp) for piezometers Pz2 and Pz3 (located in the piezometer site - PZI) and Pz6 and Pz7 (located in the piezometer site -PZII) over the WY 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

2.4.4.3. HYDRUS – 1D simulated groundwater flux

HYDRUS – 1D predicted hydraulic conductivity (Ks) to be 1.2 x 10^{-5} m s^{-1} using pedotransfer functions and inverse modeling. Descriptive statistics for groundwater flow are shown in Table 2.6. The Ks value is the same as that reported by Valett *et al*. (1996) for a study conducted in Rio Calveras, New Mexico, in an alluvial sediment RZ. In another study conducted by Fellows *et al*. (2001) at Rio Calaveras, the average groundwater velocity was reported to be 7 x 10^{-7} m s^{-1} when the summer stream discharge was 0.0003 $m^3 s^{-1}$. Compared to those results, the difference in groundwater velocity estimated at Brushy Creek (1 x 10^{-5} m s^{-1}) may be due to higher stream discharge (0.04 $m^3 s^{-1}$) relative to that of Rio Calaveras. The ratios between groundwater velocity and stream discharge were 0.07 and 0.007 m^{-2} between Rio Calaveras and Brushy Creek, respectively, indicating that the stream discharge at Brushy Creek could be influenced more by in shallow groundwater flux, which given the karst geology of the BREA may not be surprising. Fluctuations in groundwater flow were instantaneous relative to rising limb of the stream stage hydrograph at PZI, but exhibited a lag time (approximately one day) at PZII (Figures 2.7. and 2.8.). This result could be attributable to greater groundwater flow towards the stream at PZII relative to PZI (75% versus 66%, respectively). Multiple previous studies (e.g. Wondzell and Swanson, 1996; Wroblickly *et al*. 1998; Harvey and Wagner, 2000a) reported that ground water flowed on average towards the stream from the RZ, with only slight changes in net groundwater flow direction between wet and dry months. Figure 2.8. shows that during July through October, the net change in stream flow is zero due to lack of stream flow during that period. However, groundwater flow was still observed clearly indicating presence of a substantial subsurface flow regime, below the streambed. This observation supplies basis for future investigations in karst geological regions of the central U.S.

As shown in previous work, net groundwater flow varied spatially and temporally depending on stream discharge, precipitation and evapotranspiration (as noted by Hynes, 1983). However, net groundwater flow from the RZ towards the stream showed negligible change (seasonal or otherwise) at both sites (< 1%) over the study period. These results are consistent with findings of Wondzell and Swanzon (1996) who advocated the use of more complex models (e.g. 3-D) to better characterize subtle groundwater mechanistic relationships. Similarly, Harvey and Bencala (1993) also found limited change in groundwater flux (2%) at St. Kevin Gulch, Colorado. The average linear velocity (using Equation 8 and n = 0.50) did not vary between sites PZI and PZII (2.45×10^{-5} m s^{-1}), and there was limited variations between seasons indicating relatively consistent streambed conductivity (i.e. microscopic flowpaths) to shallow groundwater over time.

Table 2.6. Descriptive statistics of modeled groundwater flow (cm d^{-1}) for sites PZI and PZII for the water year 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

Site	Modeled groundwater flow (cm d^{-1})	
	PZI	PZII
Mean	105.93	106.25
Standard Deviation	0.07	0.06
Minimum	105.74	106.03
Maximum	106.09	106.32

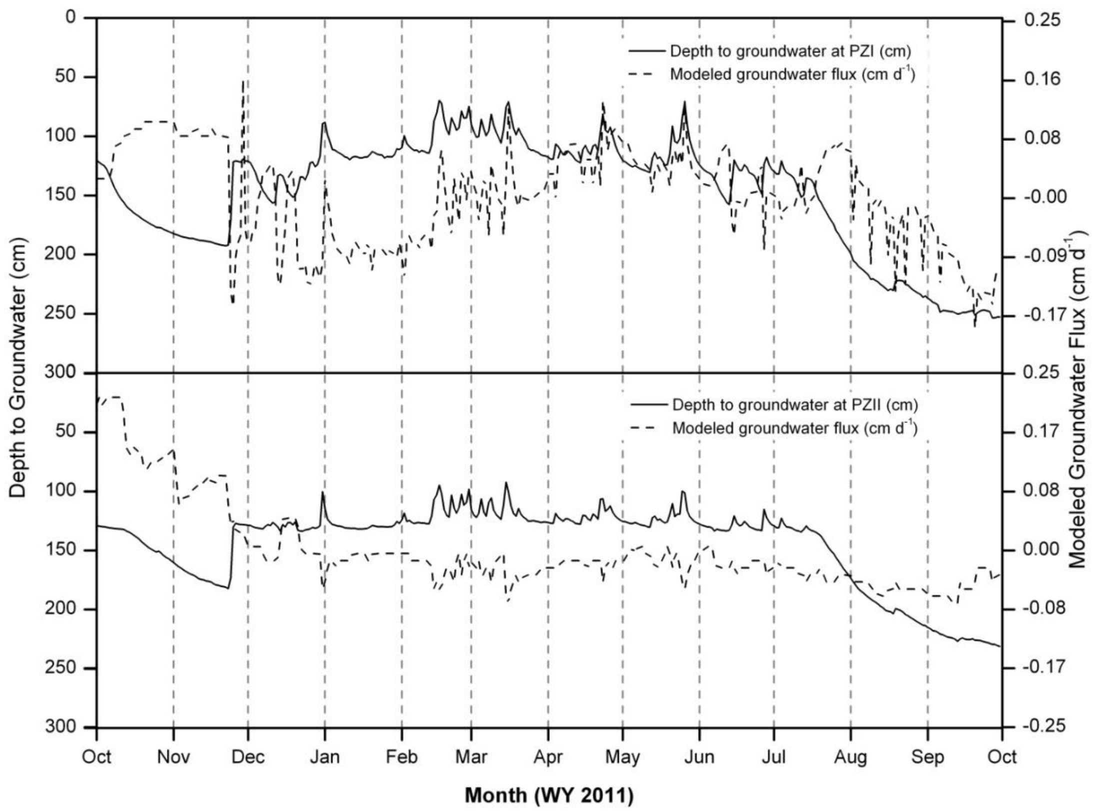

Figure 2.7. Depth to groundwater (cm) and simulated groundwater flow (cm d^{-1}) at PZI (top) and PZII (bottom) for water year 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

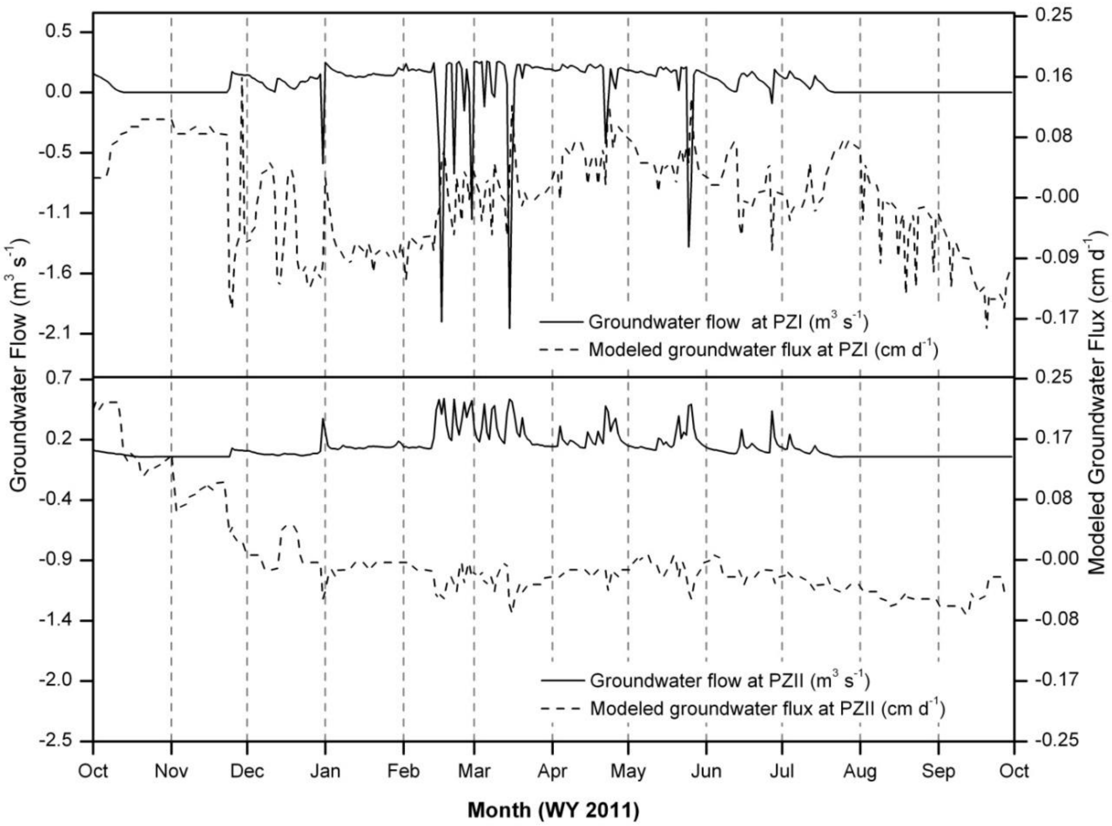

Figure 2.8. Depth to ground water flow (m^3 s^{-1}) and simulated groundwater flow (cm d^{-1}) at PZI (top) and PZII (bottom) for water year 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

2.4.5. Study limitations

Given its broad acceptance and relatively intuitive application by the management community, HYDRUS - 1D was used in this work to improve manager confidence in the model in central U.S karst watersheds. Stream flow and groundwater interactions below and within the streambed were not addressed, as data on surficial streambed geology was not available. HYDRUS - 1D simulates lateral water flux, therefore vertical water movement was not modeled. User-friendly groundwater models like HYDRUS - 1D should be developed for practitioner uses that simulate three dimensional processes (e.g.

simplified MODFLOW, HydroGeosphere, Parflow, GSFlow, and others). HYDRUS - 1D can be parameterized with finer mesh size than used in the current work. However, associated computational power, run time, and labor costs can become prohibitive for use by land managers. It is worth mentioning that calibration runs showed that the difference in results between a coarser and finer mesh size was negligible (< 2%). In the current study, piezometer spacing (2 m) was helpful to improve confidence between observed and modeled hydraulic head values. Future studies using HYDRUS – 1D with increased piezometer spacing in karst hydro-systems are warranted. However, groundwater flow between more distant piezometers should not be assumed one-dimensional (Ramos *et al*. 2011).

2.4.6. Future Directions, Closing Comments

HYDRUS – 1D successfully predicted hydraulic head values, thus illustrating the model's ability to accurately predict shallow groundwater level and flow in a central U.S karst hydrogeological ecosystem. Site-specific soil hydraulic parameters are necessary for accurate model runs (Ramos *et al*. 2011; Chen, 2007). Therefore, future studies that model a larger area should include additional observations nodes and finer discretization of model domains. In the current study, HYDRUS – 1D was able to predict groundwater flow using a minimum number of key soil and physical parameters including Ks, soil texture, soil depth, precipitation and hydraulic head. Quantification of those key parameters in the current study showed that the method is easily transferrable to other karst systems of the central U.S given sufficient key forcing are known.

Similar to the results of White (1993) from a study in Fernow streams, West Virginia, the current study results showed that groundwater velocity was 40% greater downstream at SIII-SIV (1×10^{-6} m s^{-1}) relative to SI-SII (6×10^{-7} m s^{-1}). This result was positively correlated with head differences between stream stage and groundwater level and was greatest during the hydrological maximum (winter/spring) and least during hydrological minimum (fall). The RZ of the current study had an approximate area of 150 m^2. Assuming an average aquifer thickness of 3 m and a specific yield of 0.20 for silt (Dawson and Istok, 1991; Johnson, 1967), the floodplain could store 90 m^3 of water per unit volume (450 m^3) of soil. This information is useful to land mangers wishing to formulate best management plans that also consider shallow groundwater storage processes and plant available groundwater supplies. Similarly, effective riparian forest management plans should include this information to improve contemporary timber harvest best management practices (BMPs) and reduce impacts on water quality and quantity (Verry *et al*. 2000; Burt *et al*. 2002a, 2002b; Jones and Mulholland, 2000; Welsch *et al*. 2000).

2.5. Summary and Conclusions

This work quantified shallow groundwater connectivity between a karst Ozark forested riparian zone (RZ) and a second order stream in central Missouri, U.S. Improved understanding of where and when hydrological connectivity occurs between surface and subsurface environments, via shallow groundwater exchange, is needed to improve understanding of water storage and plant uptake in many geographical settings including the central U.S. and Missouri. During the study period, on average, the entire study reach was a losing stream (19% of streamflow lost to groundwater). However, at individual study sites, the groundwater flow that accounted for stream discharge was 27% at PZI (with 37% increase in total stream flow), and therefore a gaining stream, relative to 69% at PZII (with 218% increase in total stream flow), indicating a gaining stream reach. During late summer and early fall, stream flow was greatly influenced by groundwater flow (70 to 50% of the stream flow was groundwater input). Conversely, during high precipitation events, stream water infiltrated the RZ and increased groundwater storage, as shown by a decrease in depth to groundwater by 41%. Due to the silty sand deposits and karst geology present in the study sites, shallow groundwater response was rapid (within a couple of hours). HYDRUS – 1D results were '*Very Good*' (NS = 0.95, r^2 = 0.99, RMSE = 2.38 cm and MD =1.3 cm) in terms of estimating groundwater depth and flow in the RZ.

This work provides distinct baseline hydrologic and groundwater data that will aid future investigations in karst hydrogeological forested riparian zones of the central U.S. Increasingly, models are used to predict the hydrology of small-scale watersheds and their potential hydrologic response to disturbance (Alila and Beckers, 2001; Tague and Band, 2001). However, field data and digital topographic data necessary for modeling could become laborious and costly. Results from this work show that with limited input parameters net groundwater flux can be accurately predicted leading to reasonable computations of groundwater storage. Results indicate that HYDRUS – 1D should be considered a reliable management tool (following proper calibration and validation) for establishing groundwater resources management practices for forested RZs in Missouri, the central U.S., and similar karst hydrogeological regions globally.

2.6. Acknowledgements

Funding was provided by the Environmental Protection Agency (EPA) Region 7 (Grant Number: CD-97701401-0). Results presented may not reflect the views of the EPA and no official endorsement should be inferred. Gratitude is extended to multiple members of the Interdisciplinary Hydrology Lab (IHL) of the University of Missouri. Sincere gratitude is extended to Stephen Pallardy and Kevin Hosman for climate data and valuable information about the BREA, and multiple reviewers whose comments improved the quality of the manuscript.

2.7. References

Abesser, C., Wagener, T, and G. Nuetzmann (2008), *Groundwater-Surface Water Interaction: Process Understanding, Conceptualization and Modeling*. IAHS Publication, Oxfordshire, UK.

Akerman, D, and D.E. Stein (2008), Evaluating the Effectiveness of Best Management Practices Using Dynamic Modeling. *J. Environ. Eng - ASCE*., 134, 628-639, doi: 10.1061/(ASCE)0733-9372(2008)134:8(628).

Alila, Y., and J. Beckers (2001), Using numerical modeling to address hydrologic forest management issues in British Columbia. *Hydrol. Process*., 15, 3371-3387, doi: 10.1002/hyp.1038.

Amoozegar, A., (2002), *Piezometer Method (Saturated Zone): Methods of Soil Analysis, Part 4-Physical Methods*. Soil Science Society of America Inc. Madison, Wisconsin.

Bates, P.D., *et al* (2000), Numerical simulation of floodplain hydrology. *Water Resour. Res*., 36(9), 2517-2529, doi:10.1029/2000WR900102.

Belden, A. C., and S. G. Pallardy (2009), Successional trends and apparent Acer saccharum regeneration failure in an oak-hickory forest in central Missouri, USA, *Plant Ecol*., 204, 305-322, doi: 10.1007/s11258-009-9593-4.

Bosch, J. (1979), Treatment effects on annual and dry period streamflow at Cathedral Peak, *South African Forestry Journal*., 108, 29-38, doi: 10.1080/00382167.1979.9630490.

Braca, G. (2008), Stage-discharge relationships in open channels: Practices and problemsRep., FORALPS Technical Report 11. Universita degli Studi di Trento, Dipartimento di Ingegneria Civile e Ambientale, Trento.

Brunke, M., and T. Gonser (1997), The ecological significance of exchange processes between rivers and groundwater, *Freshw. biol.*, 37, 1-33, doi: 10.1046/j.1365-2427.1997.00143.

Burt, T. P., L. S. Matchett, K. W. T. Goulding, C. P. Webster, and N. E. Haycock (1999), Denitrification in riparian buffer zones: the role of floodplain hydrology, *Hydrol. Process*., 13, 1451-1463.

Burt, T., G. Pinay, F. Matheson, N. Haycock, A. Butturini, J. Clement, S. Danielescu, D. Dowrick, M. Hefting, and A. Hillbricht-Ilkowska (2002a), Water table fluctuations in the riparian zone: comparative results from a pan-European experiment, *J. Hydro.*, 265, 129-148, doi: 10.1016/S0022-1694(02)00102-6.

Burt, T., P. Bates, M. Stewart, A. Claxton, M. Anderson, and D. Price (2002b), Water table fluctuations within the floodplain of the River Severn, England, *J. Hydrol.*, 262, 1-20., doi: 10.1016/S0022-1694(01)00567-4.

Carter, R.W., and I.E. Anderson (1963), Accuracy of current meter measurements, *Am. Soc. Civil Eng. J.*, 89, 105-115.

Castro, N. M., and G. M. Hornberger (1991), Surface-subsurface water interactions in an alluviated mountain stream channel, *Water Resour. Res*., 27, 1613-1621.

Chen, X., (2007), Hydrologic connections of a stream-aquifer-vegetation zone in south-central Platte River valley, Nebraska, *J. Hydrol*., 333, 554-568, doi: 10.1016/j.jhydrol.2006.09.020.

Critchfield, H. J., (1966), *General climatology*. Prentice-Hall, Englewood Cliffs, New Jersey.

Dages, C., M. Voltz, and P. Ackerer (2008), Parameterization and evaluation of a three-dimensional modeling approach to water table recharge from seepage losses in a ditch, *J. Hydrol*., 348, 350-362, doi: 10.1016/j.jhydrol.2007.10.004.

Dahm, C. N., N. B. Grimm, P. Marmonier, H. M. Valett, and P. Vervier (1998), Nutrient dynamics at the interface between surface waters and groundwaters, *Freshw. Biol.*, 40, 427-451, doi: 10.1046/j.1365-2427.1998.00367.

Darcy, H., (1856), *Principles to follow and formulas to be used in the question of the distribution of water*. Public foundations of the city of Dijon.

Davis, S.N., (1969), Porosity and permeability of natural materials, in R. J. M. De Wiest (Eds.), *Flow Through Porous Media*, Academic Press, New York, 53-89.

Dawson, K. J., and J. D. Istok (1991), *Aquifer testing: design and analysis of pumping and slug tests*, CRC Press, Michigan.

Dottori, F., M.L.V. Martina, and E. Todini (2009), A Dynamic Rating Curve Approach to Indirect Discharge Measurement. *Hydrol. Earth Sys. Sci*., 13, 847-863.

Fellows, C. S., H.M. Valett, and C.N. Dahm (2001), Whole-stream metabolism in two montane streams: Contribution of the hyporheic zone, *Limnol. Oceanogr*., 46, 523-531.

Freeze, R. A., and J.A. Cherry (1979), *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Garrett., H.E., and G.S. Cox (1973), Carbon dioxide evolution from the floor of an oak-hickory forest, *Soil Sci. Soc. Am. Pro*., 37, 641-644.

Gu, L., T. Meyers, S. G. Pallardy, P. J. Hanson, B. Yang, M. Heuer, K. P. Hosman, Q. Liu, J. S. Riggs, and D. Sluss (2007), Influences of biomass heat and biochemical energy storages on the land surface fluxes and radiative temperature, *J. Geophys. Res.*, 112, 1-11, doi: 10.1029/2006JD007425.

Harvey, J. W., and K. E. Bencala (1993), The effect of streambed topography on surface-subsurface water exchange in mountain catchments, *Water Resour. Res.*, 29, 89-98.

Harvey, J., and B. Wagner (2000a), Interactions between Streams and their subsurface Hyporheic Zone, in Jones, J.J., and Mulholland, P.J. (Eds.), *Streams and Ground waters*. Elsevier Publishing Co., San Diego, CA.

Harvey, J., and B. Wagner (2000b).The physical template: Hydrology, Hydraulics, and Physical structure, in Jones, J.J., and Mulholland, P.J. (Eds.), *Streams and Ground waters*, Elsevier Publishing Co, San Diego, CA.

Hughes, F. M. R. (1990), The influence of flooding regimes on forest distribution and composition in the Tana River floodplain, Kenya, *J. Appl. Ecol*., 27, 475-491.

Hurst, C. A., P. J. Thorburn, D. Lockington, and K. L. Bristow (2004), Sugarcane water use from shallow water tables: implications for improving irrigation water use efficiency, *Agr. Water Manage.*, 65, 1-19. doi: 10.1016/S0378-3774(03)00207-5.

Hynes, H.B.N., (1983), Groundwater and stream ecology. *Hydrobiologia*. 100, 93-99.

Johnson, A.I., (1967), *Specific yield — compilation of specific yields for various materials*. U.S. Geological Survey Water Supply Paper, 74 -88.

Jones, J.B., and P. J. Mulholland (2000a), *Streams and Groundwater*. Elsevier Publishing Co., San Diego, CA., 120-190.
Jones, J.B., and P. J. Mulholland (2000b), *Streams and Wetlands*. Academic Press, New York, 50-73.
Katsuyama, M., H. Shibata, T. Yoshioka, T. Yoshida, A. Ogawa, and N. Ohte (2009), Applications of a hydro-biogeochemical model and long-term simulations of the effects of logging in forested watersheds, *Sustain. Sci.*, 4, 179-188, doi: 10.1007/s11625-009-0079.
Keller, W. D., (1961), *The common rocks and minerals of Missouri*, University of Missouri, Columbia.
Krusekopf, H.H., and C.L. Scrivner (1962), *Soil survey of Boone County, Missouri*. U.S. Department of Agriculture and Missouri Agricultural Experiment Station.
Levia, D. F., D. E. Carlyle-Moses, and T. Tanaka (2011), *Reflections on the State of Forest Hydrology and Biogeochemistry*, Springer, London, 729-733.
Lewandowski, J., and G. Nutzmann (2007), *Surface water-groundwater interactions: hydrological and biogeochemical processes at the lowland River Spree (Germany)*, IAHS Publications-Series of Proceedings and Reports, Oxfordshire, UK, Report -321, 30-38.
Lewandowski, J., G. Lischeid, and G. Nützmann (2009), Drivers of water level fluctuations and hydrological exchange between groundwater and surface water at the lowland River Spree (Germany): field study and statistical analyses, *Hydrol. Process.*, 23, 2117-2128, doi: 10.1002/hyp.7277.
Luo, Y., and M. Sophocleous (2010), Seasonal groundwater contribution to crop-water use assessed with lysimeter observations and model simulations, *J. Hydrol.*, 389, 325-335., doi: 10.1016/j.jhydrol.2010.06.011.
Maest, A.S., J.R. Kuipers, C.L. Travers, and D.A. Atkins, D.A (2005), *Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties, and State-of-the-Art*, Kupiers and Associates, Montana.
Marzolf, E. R., P. J. Mulholland, and A. D. Steinman (1994), Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams, *Can. J. Fish. Aquat. Sci*., 51, 1591-1599, doi: 10.1139/f94-158.
McDonald, M. G., A. W. Harbaugh, and S. Book (1988), *A modular three-dimensional finite-difference ground-Water flow model*, in Techniques of Water-resources Investigations of the United States Geological Survey, Book 6, Chapter A1, 586.
Moriasi, D. N., J. G. Arnold, M. W. Liew, R. L. Bingner, R. D. Harmel, and T. L. Veith (2007), Model evaluation guidelines for systematic quantification of accuracy in watershed simulations, *Transactions of the ASABE*, 50, 885-900.
Mulholland, P. J., E. R. Marzolf, J. R. Webster, D. R. Hart, and S. P. Hendricks (1997), Evidence that hyporheic zones increase heterotrophic metabolism and phosphorus uptake in forest streams, *Limnol. Oceanogr.*, 443-451.
Nash, J. E., and J. Sutcliffe (1970), River flow forecasting through conceptual models part I—A discussion of principles, *J. Hydrol.*, 10, 282-290, doi: 10.1016/0022-1694(70)90255-6.

Ocampo, C. J., M. Sivapalan, and C. Oldham (2007), Hydrological connectivity of upland-riparian zones in agricultural catchments: Implications for runoff generation and nitrate transport, *J. Hydrol.*, 331, 643-658, doi: 10.1016/j.jhydrol.2006.06.010

Pallardy, S., T. Nigh, and H. Garrett (1988), Changes in forest composition in central Missouri: 1968-1982, *Am. Midl. Nat.*, 120, 380-390.

Radcliffe, D. E., and J. Simůnek (2010), *Soil Physics with HYRDUS: Modeling Applications*. 1st Edition. CRC Press, New York, 51-99.

Ramos, T., J. Šimůnek, M. Gonçalves, J. Martins, A. Prazeres, N. Castanheira, and L. Pereira (2011), Field evaluation of a multicomponent solute transport model in soils irrigated with saline waters, *J. Hydrol*., doi: 10.1016/j.jhydrol.2011.07.016.

Reed, S.E., (2010), *Ambrosia Beetle Habitat Use, Host Use, and Influence on Early Wood Colonizing Microbes in an Oak-Hickory Forest In Forestry*. University of Missouri: Columbia, Missouri.

Richards, L. A., (1931), Capillary conduction of liquids through porous mediums, *Physics.*, 1, 318-333.

Rochow, J. J., (1972), A vegetational description of a mid-Missouri forest using gradient analysis techniques, *Am. Midl. Nat*., 377-396.

Schaap, M. G., F. J. Leij, and M. T. van Genuchten (1998), Neural network analysis for hierarchical prediction of soil hydraulic properties, *Soil. Sci. Soc. Am. J*., 62, 847-855.

Schaap, M. G., F. J. Leij, and M. T. van Genuchten (2001), Rosetta: a computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions, *J. Hydrol*., 251, 163-176., doi: 10.1016/S0022-1694(01)00466-8.

Scordo, E. B., and R. D. Moore (2009), Transient storage processes in a steep headwater stream, *Hydrol.Process.*, 23, 2671-2685, doi: 10.1002/hyp.7345.

Šimůnek, J., and A. Valocchi (2002), *Geochemical transport*. In: Dane, J.H., Topp, G.C.(Eds.), Methods of Soil Analysis, Part 1. Physical Methods. Soil Science Society of America. Madison, Wis., USA. 1511-1536.

Šimůnek, J., and M. Šejna (1999), *The HYDRUS-2D software package for simulating the two-dimensional movement of water, heat and multiple solutes in variably-saturated media*. Version 2.0, IGWMC - TPS - 53, International Ground water Modeling Center, Colorado School of Mines, Golden, Colorado, 251.

Šimůnek, J., M. Šejna, H. Saito, M. Sakai, and M. T. van Genuchten (2008), The HYDRUS-1D Software Package for Simulating the Movement of Water, Heat, and Multiple Solutes in Variably-saturated Media. Version 4.0. HYDRUS Software Series 3, Department of Environmental Sciences, University of California Riverside, Riverside, CA, USA. 315.

Šimůnek, J., O. Wendroth, and M. T. Van Genuchten (1998), Parameter estimation analysis of the evaporation method for determining soil hydraulic properties. *Soil. Sci. Soc. Am. J.*, 62, 894-905.

Sophocleous, M. (2002), Interactions between groundwater and surface water: the state of the science, *Hydrogeo. J.*, 10, 52-67, doi: 10.1007/s10040-001-0170-8.

Strahler, A., (1952), Hypsometric (area-altitude) analysis of erosional topography, *Bull.Geol. Soc. Am*, 63, 1117-1142.

Tabacchi, E., L. Lambs, H. Guilloy, A. M. Planty-Tabacchi, E. Muller, and H. Decamps (2000), Impacts of riparian vegetation on hydrological processes, *Hydrol. Process*., 14(16-17), 2959-2976.

Tague, C., and L. Band (2001), Evaluating explicit and implicit routing for watershed hydro-ecological models of forest hydrology at the small catchment scale, *Hydrol. Process.*, 15(8), 1415-1439., doi: 10.1002/hyp.171.

US Department of Agriculture (USDA), N. R. C. S. (2009), Web Soil Survey.

USGS (United States Geological Survey)., (2009), Water Science for Schools. http://ga.water.usgs.gov/edu/.

Valett, H. M., S. G. Fisher, and E. H. Stanley (1990), Physical and chemical characteristics of the hyporheic zone of a Sonoran Desert stream, *J. N. Am. Benthol. Soc*., 9, 201-215.

van Genuchten, M. T., (1980), A closed-form equation for pre- dicting the hydraulic conductivity of unsaturated soils, *Soil. Sci. Soc. Am. J*., 44, 892-898.

Verry, E. S., (2000), Water Flow in Soils and Streams: Sustaining Hydrologic Function, in *Riparian area management: themes and recommendations of the Continental Eastern United States*, edited by E. S. Verry, J. W. Hornbeck and C. A. Dolloff, 99-124, CRC- Lewis Publishers Washington D.C.

Welsch, D. J., J. W. Hornbeck, E. S. Verry, C. A. Dolloff, and J. G. Greis (2000), Riparian area management: themes and recommendations of the Continental Eastern United States, in *Riparian management in forests of the continental eastern United States*, edited by E. S. Verry, J. W. Hornbeck and C. A. Dolloff, 324-325, CRC- Lewis Publishers Washington D.C.

Willmott, C. J., (1981), On the validation of models. *Phys. Geogr*., 2, 184-194.

Wondzell, S. M., and E. J. Swanson (1996), Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream I: Hydrologic processes, *J. N. Am. Benthol. Soc.*, 15, 3-19.

Wroblicky, G. J., M. E. Campana, H. M. Valett, and C. N. Dahm (1998), Seasonal variation in surface-subsurface water exchange and lateral hyporheic area of two stream-aquifer systems, *Water Resour. Res.*, 34, 317-328, doi: 10.1029/97WR03285.

Young, F. J., C. A. Radatz, and C. A. Marshall (2003), *Soil Survey of Boone County*, Missouri Natural Resources Conservation Service, 25 – 35.

Yu, P., V. Krysanova, Y. Wang, W. Xiong, F. Mo, Z. Shi, H. Liu, T. Vetter, and S. Huang (2009), Quantitative estimate of water yield reduction caused by forestation in a water-limited area in northwest China, *Geophys. Res. Lett*., 36, L02406, doi: 10.1029/2008GL036744.

CHAPTER III: NUTRIENT CONCENTRATION RELATIONSHIPS OF STREAM AND SHALLOW GROUNDWATER IN A CENTRAL U.S. OZARK BORDER FOREST

3.0. Abstract:

Information pertaining to spatiotemporal variations in surface water (SW) – shallow groundwater (GW) nutrient concentrations is critical to accurately predict stream ecosystem responses to disturbance and management practices. However, that information remains greatly limited in the karst geological region of the central United States (U.S.). Nitrate (NO_3^-), total phosphorous (P), potassium (K) and ammonium (NH_4^+) concentrations were monitored between SW and neighboring riparian zone GW over the 2011 water year in an Ozark border mixed-hardwood forest of mid-Missouri, U.S. Annual average SW NO_3^-, P, K and NH_4^+ concentrations were 0.53, 0.13, 3.29 and 0.06 mg L^{-1} respectively. Nine meters from the stream, annual average concentration for GW NO_3^- was 0.01 mg L^{-1}, while P, K and NH_4^+ concentrations were 0.03, 1.7 and 0.04 mg L^{-1} respectively. Hyperbolic model results used to quantify hydrological controls on

stream water nutrient concentrations indicated that NO_3^- and K exhibited dilution behavior while NH_4^+ had a concentration effect and P was hydrologically constant. Despite distinct physiographic differences, observed seasonal NO_3^- concentration patterns of winter maxima and summer minima in SW (1.164 and 0.133 mg L^{-1}) and GW (0.019 and 0.011 mg L^{-1}) were similar to previous U.S. studies in hardwood forests. Results indicate that despite the relatively low residence time , lower concentrations of nutrients in GW relative to SW suggest that shallow GW in karst geology may play a critical role in removing and retaining nutrients from streams in karst hydro-systems of the central U.S.

3.1. Introduction

Stream and shallow groundwater nutrient dynamics are largely regulated by water flow in the stream water (SW)-shallow groundwater (GW) mixing zone, and are influenced by variations in climate and geomorphological conditions including sinuosity and width to depth ratios (Ford and Williams, 2007; Levia *et al*., 2011; Mahler *et al*., 2008). Variations in soil physical properties and geology (e.g. hydraulic conductivity, porosity, and soil moisture) can similarly restrict or promote subsurface water flow thereby influencing SW-GW nutrient transport dynamics (Dahm *et al*., 1998). Given these complexities, it is not surprising that variations in SW-GW nutrient concentrations can be highly spatially and temporally variable (Dahm *et al*., 1998). Therefore, before stream nutrient load estimates can be calculated, frequent SW-GW nutrient concentration monitoring is necessary to capture spatiotemporal variations (as represented in Peterjohn and Correll (1984), Mayer *et al*. (2005) and in a review by Hill (1996)).

In a review of studies that quantified spatial variations in SW nutrient concentrations, Ensign and Doyle (2006) reported that in-stream uptake of nutrients, for example, nitrate and phosphorus are important in watersheds in which nutrient export in stream flow is less than terrestrial nutrient inputs to the stream. Ensign and Doyle (2006) compared 52 articles, published between the years 1981 – 2006, and reported that the average interquartile uptake length (average distance traveled by a nutrient in inorganic phase prior to uptake) was 36 to 2917 m for ammonium, 102 to 758 m for nitrate and 32 to 394 m for phosphorus, respectively. Ensign and Doyle (2006) further noted that the in-stream nutrient uptake length also changed significantly ($p = 0.014$) with stream order, indicating that the key biogeochemical nutrient cycling pathways might differ depending on stream order. They concluded that key biogeochemical nutrient cycling pathways differ between watersheds due to variable physiography. Studies are therefore warranted that seek to quantify spatiotemporal variations in nutrient concentrations and biogeochemical connectivity of streams to adjacent riparian areas.

McClain *et al*. (1994) showed that nitrate (NO_3^-) concentration decreased from 650 to 50 μg L^{-1} after passing through the riparian subsurface in a central Amazon watershed, whereas ammonium (NH_4^+) increased from 150 to 600 μg L^{-1}. In a study investigating shallow groundwater of a riparian zone in a Puerto Rican rain forest, Mc Dowell *et al*. (1992) compared results to an upland site noting a decrease in NO_3^- of 500 to 9 μg L^{-1}, and an increase in the ammonium concentration from 30 to 500 μg L^{-1}. Rapid declines in NO_3^- concentration between uplands and riparian zones were noted in many forested and grass riparian areas (Lowrance *et al*., 1984; Peterjohn and Correll, 1984; Haycock and Pinay, 1993). Peterjohn and Correll (1984) estimated that a 50 m riparian forest buffer in Maryland removed 11 kg of organic nitrogen, 0.83 kg of ammonium, 2.7 kg of nitrate, and 3 kg of total phosphorus over a one year period, indicating the need to couple riparian forests and managed habitats in order to reduce diffuse pollution. Niyogi *et al*. (2010) noted seasonal variations in stream water average nutrient concentration levels (300 and 0.91 μg m^{-2} s^{-1}during the fall and summer, respectively) within a 10 km long study reach in Mill Creek, Missouri, highlighting the need to quantify seasonal variations of in-stream nutrient concentrations to preserve stream water quality. Hill (1996) reviewed NO_3^- concentration levels from 20 watersheds concluding that 70% of riparian zones had NO_3^- concentrations that were 90% lower than those in the stream. Hill (1996) also reported that the current uncertainties in understanding riparian zone shallow groundwater nutrient cycling stem from an inadequate understanding of the hydrologic regime, stressing the need for research in varying landscape hydrogeology and climates including additional nutrients (e.g. phosphorous, potassium, and ammonium).

Scientists have demonstrated that depletion of GW NO_3^- in forested riparian zones occurs over short distances (Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985, Haycock and Burt, 1993). Peterjohn and Correll (1984) showed that 90% of NO_3^- was depleted from the subsurface groundwater within 19m of a deciduous forest riparian zone in Maryland in U.S. Similarly, Jacobs and Gilliam (1985) indicated that 95% of NO_3^- was removed (by plant uptake) from the subsurface groundwater within 20m of a deciduous forest riparian zone in North Carolina in the U.S. Study sites of Jacobs and Gilliam (1985) and Peterjohn and Correll (1984) had an impermeable layer within 3m from the ground resulting in a dominant shallow lateral groundwater flow path. Both investigations observed no increase in GW NH_4^+ or organic N, indicating that the NO_3^- loss was not due to transformation of NO_3^- but loss due to rapid water movement that can transport NO_3^- to deeper aquifers or to stream water. In a review on SW-GW nutrient interaction studies across the U.S, Hill (1996) indicated that the GW NO_3^- loss within narrow riparian zones with widths 15 to 20m, and dominant lateral shallow groundwater flow paths should be primarily due to geochemical nutrient cycling pathways rather than biochemical pathways. However, studies that quantify spatiotemporal SW-GW nutrient concentration variations in environments that exhibit geochemical nutrient cycling pathways are limited (Hill, 1996; Burt *et al*., 2010; Levia *et al*., 2011).

Nitrogen (N), phosphorus (P) and potassium (K) are considered critical and often limited nutrients for primary production in forested riparian zones and depends on the landscape (Cassidy and Jordan, 2011; Jones and Mulholland, 2000; Levia *et al*., 2011). In contrast to N, P and K do not exist in gaseous form and are largely derived from mineral weathering (Levia *et al*., 2011). Likens and Borman (1977) reported that 99 and 89% of total P and K input was from mineral weathering, while 100% of N input was from atmospheric deposition in the Hubbard Brook Experimental Forest in New York, U.S. Researchers have quantified the influence of stream discharge on K and P input to the watershed (Salmon *et al*. 2001, Stelzer and Likens, 2006; Barco *et al*., 2012) and thus attempted to quantify variations in mineral weathering rates with stream flow variation. Salmon *et al*. (2001) showed that P was hydrologically constant within study sites (i.e. there was no net change in the P concentration level with increases in stream discharge) at Chiloe National Park in Chile. In a review that used 14 U.S. river discharge data sets, Stelzer and Likens (2006) showed a net increase in total P with increase in discharge. The observed increase in total P was attributed to geochemical pathways, in particular runoff transport of P that is adsorbed to sediments.

Despite compelling evidence that a range of additional parameters (i.e. nutrients, physical parameters, and particulate contaminant cycles) are subject to influence by the biogeochemical and hydrological processes occurring within the riparian zone (Burt *et al*., 2010; Vidon *et al*., 2010; Burgin and Hamilton, 2007), SW-GW nutrient studies have focused primarily on nitrogen cycling. As a result, the role of SW-GW exchange dynamics in modifying stream nutrient loading within forested watersheds remains elusive (Mulholland, 1992; Mulholland and Webster, 2010; and Burt *et al*., 2010).

Scientists have used various time-periods to quantify physical processes that influence SW-GW interactions of a region. Necessary data for such studies is often very difficult to obtain, and requires a great deal of field based infrastructure and labor. Recent studies showed that short time series (from weeks to one year) was more than adequate to understand regional SW-GW interactions. Pretty *et al*. (2006) used one year of hydrologic and nutrient data to quantify biogeochemical processing rates in the riparian zone on the River Lambourn in Berkshire, UK. They indicated that the nutrient processing was primarily due to biological uptake, despite the presence of a semi-karst geology. Ocampo *et al*. (2006) used six months of hydrologic data to estimate upland-riparian zone hydrological connectivity in Susannah Brook catchment in Perth, WA. Their results showed that SW-GW hydrologic connectivity is accompanied by a sharp increase in hydraulic gradient towards the stream. Chen (2007) used one month of hydrologic data to quantify SW-GW connections in a study located along the Platte River in Nebraska. Chen (2007) showed that SW-GW interactions at the Platte River are highly influenced by aquifer thickness, vertical anisotropy and aquifer hydrologic connectivity. The aforementioned studies were successful in using relatively short time periods of hydrologic and nutrient data to understand SW-GW interactions. Therefore, the current study used short time periods of SW-GW hydrologic and nutrient data to improve mechanistic process understanding.

Studies that quantify SW-GW nutrient concentration relationships will aid riparian forest management practices by identifying temporal variations in stream nutrient loading (Burt *et al*., 2010) and help predict water quality alterations subsequent to specific management practices (Levia *et al*., 2011; Jones and Mulholland, 2000). Identification of nutrient loading trends will aid in the formulation of management plans intended to mitigate excess stream nutrient loading (e.g. by adjusting riparian zone buffer width and density), and excess nutrient leaching (e.g. by installing drainage systems) (Mayer *et al*., 2005). Given recent advancements in scientific tools and numerical models (Levia *et al*., 2011), reliable science-based riparian zone management plans are often possible. However, information gleaned from SW-GW nutrient studies remain limited in many regions, including the central mid-western region of the U.S., particularly in Ozark border forested ecosystems. Kirchner *et al*. (2004), Jones (2007), and Cassidy and Jordan (2011) showed the inadequacy of coarse sampling approaches for estimating nutrient loading in SW-GW interactions, thereby showing the need for higher resolution (spatial and temporal) studies. Given the aforementioned needs, the following work uses high-frequency water quality monitoring in an Ozark border forest to quantify spatiotemporal variations in SW-GW nutrients (NO_3^-, total P, K, and NH_4^+).

Specific objectives of this study included the following: (1) to determine stream water and shallow groundwater nutrient concentrations for NO_3^-, P, K, and NH_4^+; (2) to characterize spatial trends in nutrient concentrations, (3) to characterize temporal patterns in nutrient concentrations, and 4) to quantify influence of stream discharge on stream water nutrient concentrations using a modified version of the hyperbolic dilution model proposed by Johnson *et al*. (1969). The current study will provide greatly needed baseline information that will inform scientists and help guide land management decisions.

3.2. Study Site

This study was conducted on two reaches of Brushy Creek within the Thomas S. Baskett Wildlife Research and Education Area (BREA), located in the Ozark border region of south-central Missouri, U.S. (Pallardy *et al*., 1988) (Figure 3.1.). The BREA is a wildlife reserve managed by the University of Missouri (Rochow, 1972) and has remained undisturbed (i.e. no forest harvest) for more than 60 years. The climate in the BREA is classified as humid-continental (Critchfield, 1966). Mean January and July temperatures are -2.2 °C and 25.4 °C, respectively. Mean annual precipitation is 1,037 mm, recorded between 1971 and 2010 at the Columbia Regional Airport located 8 km north of the BREA (Belden and Pallardy, 2009). The average annual temperature and precipitation measured at the on-site Ameriflux tower from 2005-2010, was 13 °C and 930 mm, respectively, versus 12.9 °C, and 1,089 mm at the Columbia Regional Airport during the same time period. Brushy Creek is a second order stream (Strahler, 1952) with an average slope of 0.94%. Brushy Creek joins Cedar Creek, 4 km south of the BREA, subsequent to the drainage of a watershed of an approximate area of 9.17 km^2. During drier periods of the year, Brushy Creek flow is seasonally intermittent from a combination of event-based precipitation and shallow groundwater seepage.

The BREA's dominant soils are Weller silt loam and Clinkenbeard clay loam (Rochow, 1972) while the underlying limestone geology is of Ordovician and Mississippian age. Riparian zone soils consist of Cedargap and Dameron soil complexes (USDA soil map unit 66017 as listed in NLCD (2001) by Fry *et al*. (2009)). The BREA soils are well drained and exhibit an average bulk density of 1.2 to 1.4 g cm^{-3} (Young *et al*., 2001). Current land use ranges from second growth forests in the southern portion to pastures in the northern portion. The watershed consists of 2.6% suburban land use, 17.9% cropland, 33% grassland, 43.2% forest, and 3.3% open water and wetlands (Fry *et* *al*., 2009). Vegetation consists of northern and southern division oak-hickory forest species (Rochow, 1972) including American Sycamore (*Platanus occidentalis*), American Elm (*Ulmus americana*), and Black Maple (*Acer nigrum*) dominated riparian reaches (*Belden and Pallardy*, 2009). Understory vegetation consists of Sugar Maple (*Acer saccharum*), Flowering Dogwood (*Cornus florida*), and Black Cherry (*Prunus serotina*) (Reed, 2010).

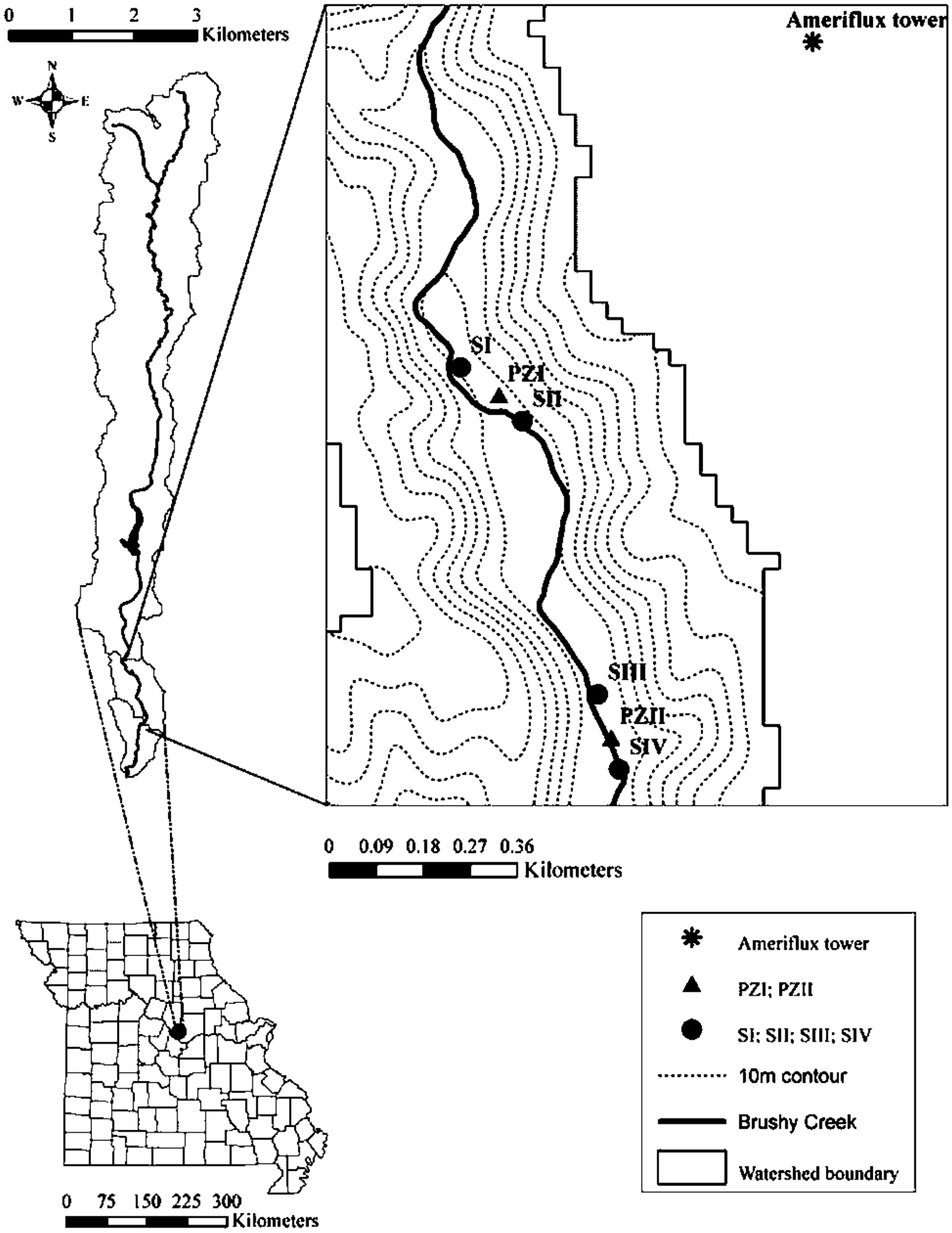

Figure 3.1. Study sites (SI-SIV) and piezometer locations (PZI, PZII) in Baskett Wildlife Research and Education Area (BREA), along Brushy Creek, central Missouri, U.S.

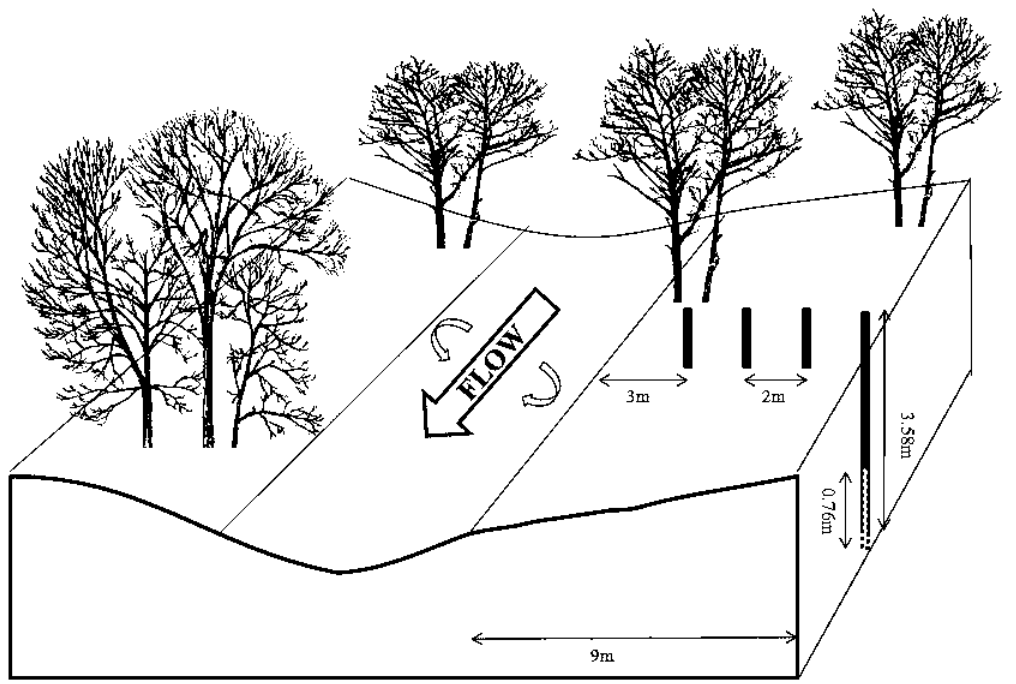

Figure 3.2. Cross section of a study site in Baskett Wildlife Research and Education Area (BREA), along Brushy Creek, central Missouri, U.S.

3.3. Methods

3.3.1. Instrumentation and data-collection

Climate data were collected from an on-site AmeriFlux tower, located at an elevation of 238 m, on a forested ridge (Figure 3.1.). Climate data were obtained via public ftp server: (ftp://ftp.atdd.noaa.gov/pub/GEWEX/2010/mo/). Precipitation was measured using a TE525 Texas Electronics rain gauge (error ± 1%) and air temperature was measured with a Vaisala HMP45C-L temperature-relative humidity sensor (error ± 0.2°C).

Four in-stream stilling wells were installed (hereafter referred to as SI – SIV) in 2010 to monitor stage and estimate stream discharge before and after each piezometer grid (Figure 3.1.). Stilling wells were equipped with Solinst® Levelogger Gold pressure transducers (error ± 0.003 m) and recorded stream stage at five minute intervals. Streamflow rating curves were determined from measured stage-discharge relationships using the stream cross section method (Dottori *et al.*, 2009) with a Marsh-McBirney ® Flo-Mate flow meter (error ± 2%).

Between SI and SII, four piezometers were installed along a transect (Piezometer Site I, hereafter referred to as PZI) that extended from 3 m from the stream edge to 9 m into the riparian zone (Figure 3.1.). PZI was located at 38°44' N latitude and 92°12' longitude at an elevation of 177 m along the east-west stream reach approximately 90 m long and 15 m wide at bankfull. In a similar manner, Piezometer Site II (PZII) was located 660 m S-SE of PZI at 38°43' N latitude and 92°12' W longitude at an elevation of 174 m along an approximate north-south stream reach 157 m long and 10 m wide at bankfull. Each 3.58 m drive-point piezometer with a 4 cm inner diameter and a 0.76 m slotted screen at the end was equipped with a Solinst® Levelogger Gold pressure transducer programmed to log water level at five minute intervals (Figure 3.2.).

Weekly stream water grab samples were collected during the 2011 WY near each of the four stream stage monitoring sites (SI – SIV, n = 4) and from each piezometer well (n = 8) and analyzed for nutrient concentrations. Piezometers were purged (1000 ml) using a handpump prior to sample collection. Stream water samples were manually collected, according to USEPA water sampling protocol (USEPA, 2000), and stored in disposable sterile 100 ml Whirl – Pak® bags upon collection. Water pH, temperature (°C), conductivity (µS), total dissolved solutes (TDS in ppm), and salinity (ppm) were measured in the field at the time of sample collection using an Oakton® Multi - Parameter PCS Testr ™ (calibrated monthly). The water samples were placed on ice and transported to the lab within two hours of collection and refrigerated until analysis (less than 24 hours).

3.3.2. Data collection and analyses

3.3.2.1. Quantifying stream water flow

To relate stream stage to stream discharge, rating curves of the following form:

$$Q = a \times Z^{b} \qquad [1]$$

were developed as per Dottori *et al*. (2009), where Q is stream flow (m^3 s^{-1}), Z is stream stage (m), and a and b are coefficients determined by stream morphology within the area of the measurements, as well as the location for stage measurement data. Regular and event-based, velocity-area stream gauging was conducted. Four rating curves were established, one at each of the four stilling well locations in order to calculate the spatial variability of stream discharge along the study reach. Stream discharge spatial variability estimates can provide insight into the sources of water and the nutrients transported with the water to the stream along the study reach.

3.3.2.2. Quantifying nutrient concentration

All nutrient analyses were performed in the Interdisciplinary Hydrology Lab located in the School of Natural Resources at the University of Missouri. Weekly manual (i.e. grab) water samples were analyzed for nitrate (NO_3^-), total phosphorous (total PO_4^{3-}), potassium (K) and ammonium-N (NH_4^+) concentrations using a HACH® DR 2800™ spectrophotometer. Nitrate was measured using an USEPA approved Dimethylphenol Method TNTplus™ 836 (with detection limits of 0.23 – 13.50 mg L^{-1}); while total phosphorus, potassium and ammonium were measured using Total Ascorbic Acid Method TNTplus™ 843 (with detection limits of 0.15 – 4.50 mg L^{-1}), TNT Tetraphenylborate Method Powder Pillows (with detection limits of 1.0 – 7.0 mg L^{-1}) and Salicylate Method TNTplus™ 830 (with detection limits of 0.015 – 2.000 mg L^{-1}), respectively. NO_3^- ions in solutions containing sulfuric and phosphoric acids react with 2, 6-dimethylphenol to form 4-nitro-2, 6 dimethylphenol, which is then tested for NO_3^- using wavelength of 345nm. For total PO_4^{3-}, orthophosphate reacts with molybdate in an acid medium to produce phosphate-molybdate complex. Ascorbic acid then reduces the complex to give an intense molybdenum blue hue, which is then measured using wavelength of 880 nm. For measuring K, sodium tetraphenylborate reacts with K to form potassium tetraphenylborate, the resulting turbidity is then measured using wavelength of 650 nm. NH_4^+ ions react with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside to form indophenol, which is measured using a 690 nm wavelength. Detailed procedures of the aforementioned methods is available at www.hach.com (HACH, 2007).

Phosphorus data from October to December of 2010 were removed from the data set due to defective analytes yielding test results that were over the measurement range (greater than 4.5 mg L^{-1}). In recent years, Beale's Ratio estimator (Beale, 1962) has been shown to be successful for predicting missing phosphorus data (Wang *et al*., 2011;

Kulasova *et al*., 2012; Richards, 2000). The Beale's Ratio is given as follows (Beale, 1962):

$$\frac{I_a}{Q_a} = \frac{I_o}{Q_o} \quad [2]$$

where I is the concentration and Q is the discharge. The subscript a represents annual average values for the period of study. The subscript o represents the date for which the concentration must be estimated. The Beale's Ratio estimator assumes that the annual ratio of the concentration to the flow for a study site is similar to the ratio of the concentration to the flow on individual days (Wang *et al*., 2011; Kulasova *et al*., 2012; Richards, 2000). Given Beale's Ratio estimator's successful application in previous studies, the model was used in the current work to fill phosphorus data gaps.

3.3.2.3. The relationship between nutrient concentrations and stream flows

The hyperbolic dilution model proposed by Johnson *et al*. (1969) has been widely used to describe the response of stream nutrient concentrations to changes in stream flow (Barco *et al*., 2012; Stelzer and Likens, 2006; and Salmon *et al*., 2001). Spatiotemporal trends in nutrient concentration verses discharge relationships were characterized using the Johnson *et al*. (1969) model, as follows:

$$C = \left[\frac{C_\delta}{1 + (\beta \times Q)} \right] + C_\alpha \qquad [3]$$

where C is the solute concentration in stream water, C_α is the nutrient concentration in stream water during periods of high discharge, C_δ is the resultant slope parameter, Q is discharge, and β is a proportionality parameter. As discussed by Salmon *et al*. (2001), the aforementioned physical parameters were not mechanistically quantified. The model parameters β, C_α, and C_δ were estimated using a global nonlinear curve fitting option in Origin® software. The resulting relationships between stream discharge and stream water nutrient concentrations were then compared against hydrological control mechanisms as determined by Johnson *et al*. (1969), Barco *et al*. (2012), Stelzer and Likens (2006), and Salmon *et al*. (2001).

Hydrological controls on stream water nutrient concentrations exhibit three typical patterns with respect to stream discharge, as follows: (1) Type I – dilution, (2) Type II – enhanced hydrological access (concentration), and (3) Type III – hydrologically constant (Barco *et al*., 2012; Stelzer and Likens, 2006; and Salmon *et al*., 2001). The dilution type curve corresponds to a positive C_δ, whereas a negative C_δ corresponds to an increase in concentration with stream discharge. Nutrient dilution occurs when stream nutrient loading is lower than water delivery to the stream (Johnson *et al*. 1969). Salmon *et al*. (2001) noted that dilution is common for nutrients with a strong internal watershed source that does not linearly increase with discharge. Given the success in the use of the hyperbolic model in previous studies to identify hydrologic controls of stream nutrient concentrations (Barco *et al*., 2012; Stelzer and Likens, 2006; and Salmon *et al*., 2001), and the availability of one full year of stream and shallow groundwater flow data, the hyperbolic dilution model was validated and utilized for the current work.

3.4. Results and Discussion

3.4.1. Climate during the study period

Climate at the BREA during WY 2011 was characterized by mean air temperature of 12.5 ˚C and total precipitation of 647 mm. WY 2011 was on average cooler and drier relative to the 30 year average (1971-2012) air temperature (14.1 ˚C) and precipitation (816 mm) recorded at the on-site Ameriflux tower. The highest precipitation on a single day was 44 mm on December 31, 2010. Seasonal precipitation was 170 mm (winter = December to March), 250 mm (spring = March to June), 135 mm (summer = June to September), and 94 mm (fall = September to December). The resulting stream flow was variously ephemeral, with high flows during the spring and summer season, and drying by mid-October (Figure 3.3.).

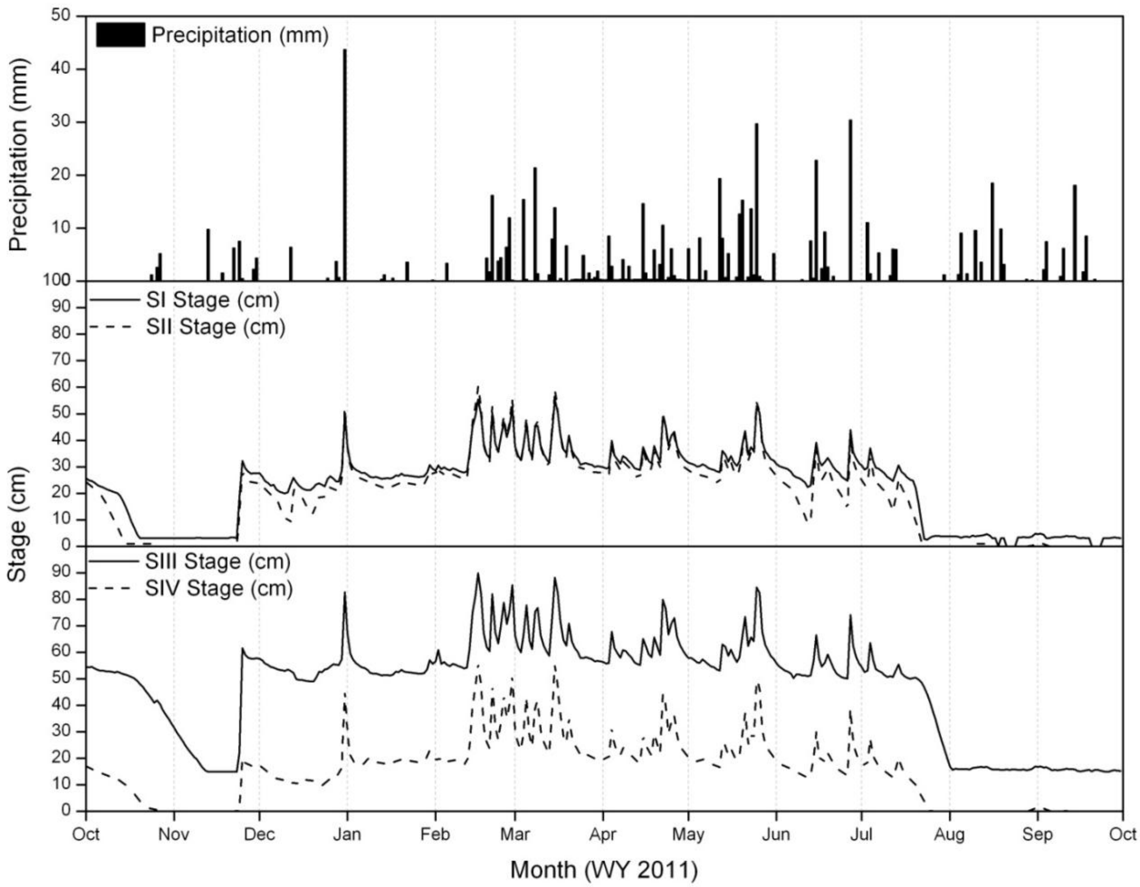

Figure 3.3. Comparison between measured precipitation (mm) and stream stage at SI to SIV (cm) during WY 2011 at the Baskett Wildlife Research and Education Area (BREA) central Missouri, U.S.

3.4.2. Streamflow

Annual stream flow at SII was 44% greater than the streamflow at SI (due to increasing GW input to SW and increasing stream length), indicating that the stream reach (between SI and SII) was, on average, a gaining stream (Table 3.1.). Similarly, average stream flow at SIV was twice (218%) that of SIII, indicating that the stream reach (between SIII and SIV) was also, on average, a gaining stream (Table 3.1.). Average daily stream flow during the study period was highest at SII (0.22 $m^3 s^{-1}$)

followed by SI (0.16 $m^3 s^{-1}$), SIV (0.13 $m^3 s^{-1}$), and SIII (0.04 $m^3 s^{-1}$) indicating that the stream was intermittently gaining and losing along the entire reach. Daily average stream discharge at SIV was higher during the winter and spring (0.25 and 0.20 $m^3 s^{-1}$) seasons, compared to the fall and summer (0.04 and 0.02 $m^3 s^{-1}$). High flow conditions were observed at all four stream gauging locations during the winter season (December to March with a total of 170 mm of precipitation). A detailed report on stream flow and shallow-groundwater flow is provided in Chinnasamy and Hubbart (in submission). Descriptive statistics of streamflow at each site are listed in Table 3.1.

Marzolf *et al*. (1994) reported average stream flow of 0.003 and 0.002 $m^3 s^{-1}$ during summer and fall seasons (i.e. one-tenth the flow of Brushy Creek, with reach length = 830 m) with groundwater flow of 1 x 10^{-4} and 2 x 10^{-4} $m^3 s^{-1}$ (i.e. one-hundredth the groundwater flow observed at SIV-SIII, Brushy creek) in Walker Branch Creek in Tennessee (reach length = 62m). The higher flow in Brushy Creek, relative to that in the Walker Branch Creek study is explained in part by larger drainage area and study reach length.

Table 3.1. Descriptive statistics of daily stream flow at four monitoring sites during water year 2011 at the BREA, central Missouri, U.S.

Site	SI ($m^3 s^{-1}$)	SII ($m^3 s^{-1}$)	SIII ($m^3 s^{-1}$)	SIV ($m^3 s^{-1}$)
Mean	0.16	0.22	0.04	0.13
Std. Dev.	0.45	0.29	0.13	0.23
Minimum	0.00	0.00	0.00	0.00
Maximum	3.80	1.78	1.22	1.59

*Sites I-IV = stilling well locations
Std. Dev. = Standard Deviation

3.4.3 Nutrient Concentrations

3.4.3.1. The spatial and temporal patterns of stream water nutrient concentrations

As anticipated, stream nutrient concentrations were spatially variable along the stream reaches of this investigation (Figure 3.4. and Tables 3.2. and 3.3.). SI had the highest NO_3^- average annual concentration (0.53 mg L^{-1}) followed by SII (0.42 mg L^{-1}), SIII (0.33 mg L^{-1}), and SIV (0.33 mg L^{-1}). A progressive downstream decline in NO_3^- (Figure 3.4., Tables 3.2. and 3.3.) concentration in the stream was likely due to a combination of dilution due to increasing stream distance (and stream flow) and shallow groundwater flow to the stream (Johnson *et al*., 1969; Barco *et al*., 2012; Stelzer and Likens, 2006; and Salmon *et al*., 2001). Nutrient concentrations may have also declined coupled to stream distance due to vegetation uptake (Levia *et al*., 2011; Burt *et al*., 2010), chemical transformation (Jones and Mulholland, 2000) and volatilization (Burgin and Hamilton, 2007). Dilution due to increase in GW contribution to stream discharge coupled to stream distance is presumed to be the greatest influence in this case, and is supported by multiple previous authors (for example, Ford and Williams, 2007; Levia *et al*., 2011; Mahler *et al*., 2008). NH_4^+followed the observed NO_3^- spatial pattern with SI and SII (0.06 mg L^{-1}), higher than SIII (0.05 mg L^{-1}) and SIV (0.04 mg L^{-1}). The PO_4^{3-} concentration was highest at SI (0.53 mg L^{-1}) followed by SII (0.42 mg L-1), SIV (0.33 mg L^{-1}), and SIII (0.33 mg L-1). K was highest at SII (3.78 mg L^{-1}) followed by SIII (3.32 mg L^{-1}), SIV (2.47 mg L^{-1}), and SI (2.28 mg L^{-1}). All observed stream water nutrient concentrations varied significantly between each other ($p < 0.001$). However, there was no significant difference ($p > 0.05$) between GW NO_3^- and $NH_4^+$and PO_4^{3-}

concentrations, all of which varied significantly ($p = 0.001$) relative to K concentration. This result shows that the shallow GW nutrients at sites PZI and PZII were influenced by similar biogeochemical processes and therefore implies that with respect to shallow GW, similar riparian zone management plans can be applied despite differences in riparian zone width (20 m), stream reach length and stream distance.

Stream nutrient concentrations varied seasonally with similar spatial trends as seasonal variations in groundwater nutrients (Table 3.3.). Stream water NO_3^- concentration was highest at all sites during the winter with 1.164, 1.088, 0.860, and 0.865 mg L^{-1} of NO_3^- detected from SI to SIV, respectively. Stream NO_3^- was lowest during the summer season with 0.285, 0.237, 0.144 and 0.133 mg L^{-1} at SI-SIV, respectively. $NH_4^+$was highest in concentration during the summer at most sites, with 0.11, 0.14, 0.06, and 0.06 mg L^{-1} at SI-SIV; and lowest in concentration during spring with 0.03 mg L^{-1} at SI to SIII and 0.02 mg L^{-1} at SIV. PO_4^{3-} was highest in concentration during winter months (when plant uptake was presumably less), with 0.18, 0.17, 0.09, and 0.08 mg L^{-1} observed at SI to SIV, respectively. Lower SW values of PO_4^{3-} were observed during late summer and early fall with 0.08, 0.06, 0.07, and 0.04 mg L^{-1} at SI to SIV, respectively. K was higher in concentration during the summer season, with 4.06, 5.32, 4.35, and 2.88 mg L^{-1} observed at SI to SIV, respectively. Lower concentrations of K were observed during the spring season with 2.76, 2.77, 2.66, and 2.43 mg L^{-1} at SI to SIV, respectively.

Concentrations of NO_3^- in stream and shallow groundwater were lower in late spring and summer. Higher NO_3^- and NH_4^+ in stream and groundwater samples were observed during winter when the stream flow and groundwater level was the highest at all sites, due to nutrient transport by water and lower plant uptake (as plant growth is limited during winter (Levia *et al*., 2011), compared to other seasons, indicating that lowering of nutrient concentration due to advection and dilution by water is the primary method for nutrient loss (Hill, 1996; Lowrance *et al*., 1984; Peterjohn and Correll, 1984; Haycock and Pinay, 1993). The late summer and early fall seasons had the lowest streamflow and groundwater levels (see chapter 2 of this dissertation for more information) corresponding to higher K concentration values and lower NO_3^- at all sites. However, NH_4^+ exhibited the least variability remaining low at all sites with the exception of summer, when a slight increase was noted at all sites. Descriptive statistics for stream water and groundwater nutrient concentrations are reported in Table 3.2. and shown in Figure 3.5. with seasonal variations listed in Table 3.3.

Table 3.2. Descriptive statistics of annual (WY 2011) average nutrient concentrations (mg L^{-1}) measured in stream water and riparian zone groundwater at the Baskett Wildlife Research and Education Area (BREA) central Missouri, U.S. for WY 2011.

Position	Statistics	Nutrient			
		Nitrate - N	Total Phosphorus	Potassium	Ammonium - N
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
Stream Water					
SI	Mean	0.53	0.13	3.29	0.06
	Std. Dev.	0.55	0.07	1.02	0.08
	Minimum	0.00	0.02	1.60	0.01
	Maximum	1.87	0.33	6.00	0.57
SII	Mean	0.42	0.11	3.78	0.06
	Std. Dev.	0.52	0.07	1.36	0.09
	Minimum	0.00	0.00	1.60	0.01
	Maximum	1.78	0.32	7.80	0.55
SIII	Mean	0.33	0.09	3.32	0.05
	Std. Dev.	0.44	0.04	1.13	0.06
	Minimum	0.00	0.00	1.40	0.01
	Maximum	1.61	0.17	5.90	0.32
SIV	Mean	0.33	0.07	2.47	0.04
	Std. Dev.	0.45	0.04	1.39	0.05
	Minimum	0.00	0.00	0.80	0.01
	Maximum	1.63	0.22	5.50	0.22
Riparian Groundwater					
PZI	Mean	0.01	0.03	1.86	0.03
	Std. Dev.	0.02	0.01	0.43	0.01
	Minimum	0.00	0.01	1.23	0.01
	Maximum	0.12	0.07	2.80	0.05
PZII	Mean	0.01	0.04	1.44	0.06
	Std. Dev.	0.03	0.02	0.78	0.03
	Minimum	0.00	0.01	0.55	0.01
	Maximum	0.20	0.10	6.27	0.13

*Sites I-IV = Stilling well locations
PZI-II = Piezometer locations
Std. Dev. = Standard Deviation

Table 3.3. Spatial and seasonal variations of average nutrient concentrations (mg L^{-1}) measured in stream water and riparian zone groundwater at the Baskett Wildlife Research and Education Area (BREA) central Missouri, U.S. for WY 2011.

Position	Season	Nitrate - N (mg L^{-1})	Total Phosphorus (mg L^{-1})	Potassium (mg L^{-1})	Ammonium - N (mg L^{-1})
Stream Water					
SI	Fall	0.231	0.08	3.08	0.04
	Winter	1.164	0.18	3.22	0.06
	Spring	0.408	0.16	2.76	0.03
	Summer	0.285	0.10	4.06	0.11
	Annual	0.522	0.13	3.28	0.06
SII	Fall	0.080	0.06	4.49	0.05
	Winter	1.088	0.17	3.32	0.06
	Spring	0.360	0.12	2.77	0.03
	Summer	0.237	0.10	5.32	0.14
	Annual	0.440	0.11	3.97	0.07
SIII	Fall	0.074	0.07	3.98	0.09
	Winter	0.860	0.12	3.18	0.05
	Spring	0.315	0.09	2.66	0.03
	Summer	0.144	0.08	4.35	0.06
	Annual	0.348	0.09	3.55	0.06
SIV	Fall	0.068	0.04	3.16	0.06
	Winter	0.865	0.11	2.31	0.05
	Spring	0.302	0.08	2.46	0.02
	Summer	0.133	0.07	2.88	0.06
	Annual	0.342	0.07	2.7	0.05
Riparian Groundwater					
PZI	Fall	0.011	0.03	1.72	0.03
	Winter	0.019	0.03	1.56	0.03
	Spring	0.006	0.03	1.79	0.02
	Summer	0.011	0.03	2.51	0.03
	Annual	0.012	0.03	1.9	0.03
PZII	Fall	0.009	0.03	1.73	0.05
	Winter	0.008	0.04	1.05	0.03
	Spring	0.020	0.03	1.14	0.06
	Summer	0.012	0.04	1.82	0.08
	Annual	0.012	0.04	1.43	0.06

*Sites I-IV = Stilling well locations and PZI-II = Piezometer locations

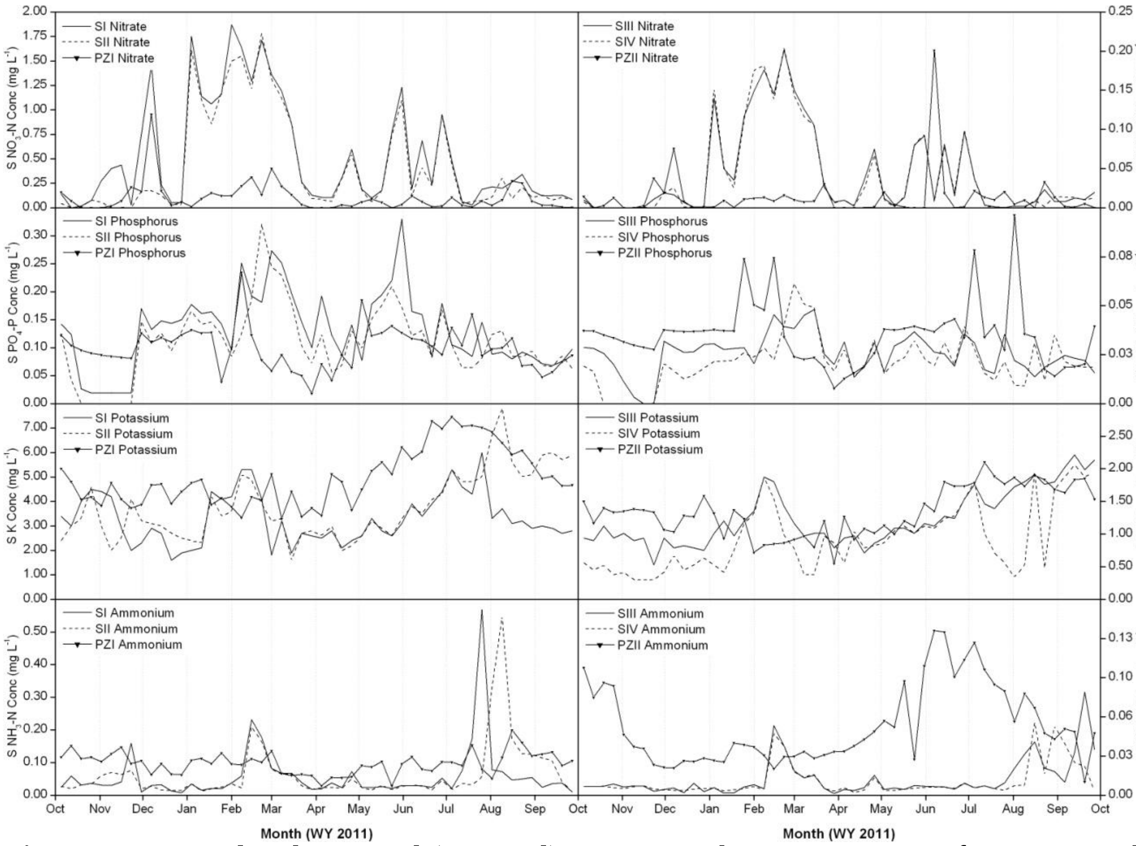

Figure 3.4. Spatial and temporal (seasonal) patterns in the concentration of nitrates, total phosphorous, potassium, and ammonium (mg L^{-1}) in stream water collected at stilling well (S = stilling well) locations (SI-SIV); and groundwater from the piezometer (PZ = piezometer) locations (PZI and PZII) observed at the Baskett Wildlife Research and Education Area (BREA) central Missouri, U.S. for WY 2011.

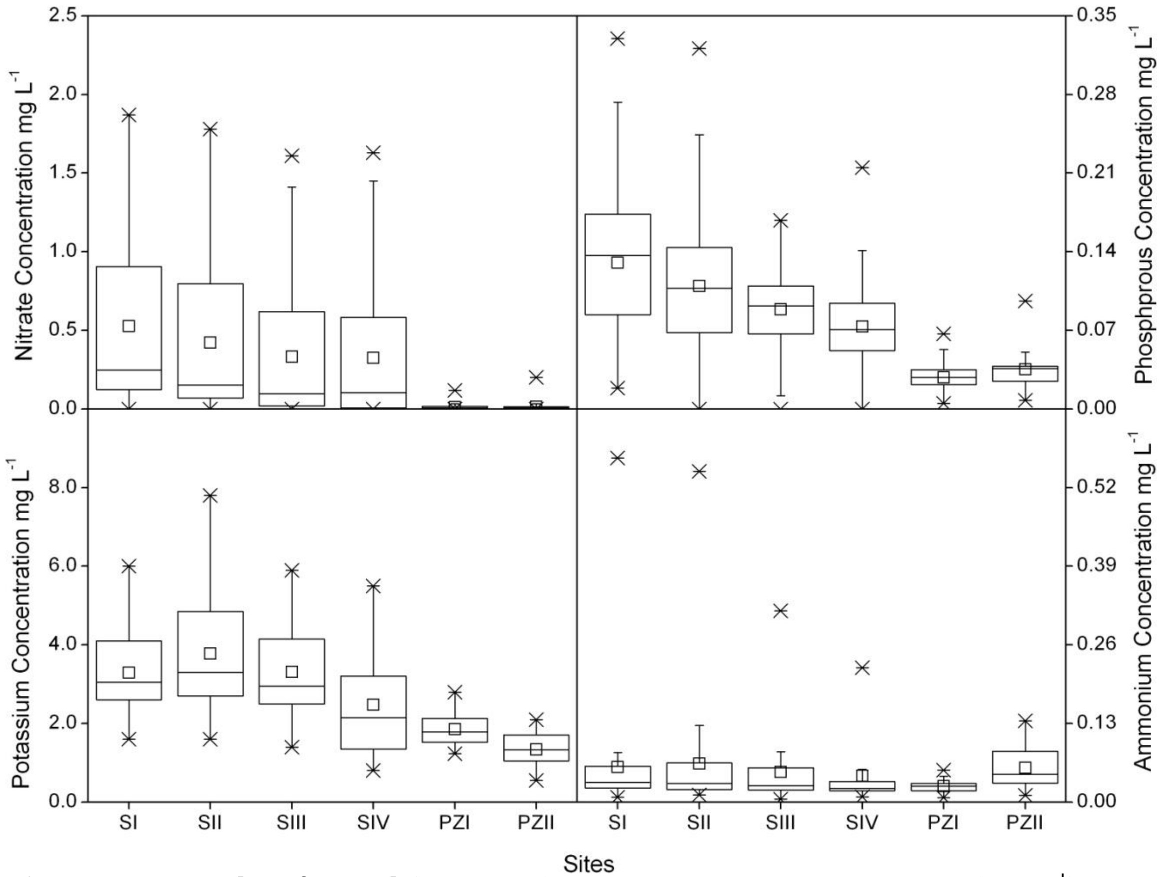

Figure 3.5. Box plot of annual (WY 2011) average nutrient concentrations (mg L^{-1}) measured in stream water and riparian zone groundwater at the Baskett Wildlife Research and Education Area (BREA) central Missouri, U.S. for WY 2011. X = 5th and 95th percentiles.

3.4.3.2. The spatial and temporal patterns of shallow groundwater nutrient concentrations

Average spatiotemporal nutrient concentrations of stream water and shallow groundwater are listed in Table 3.3. The annual average shallow groundwater NO_3^- concentration entering from the upland was 0.01 mg L^{-1} at both PZI and PZII. The annual average groundwater NO_3^- concentrations 3 m near the stream were 0.03 and 0.01 mg L^{-1} at PZI and PZII, respectively, indicating no net change in NO_3^- at PZI, and a net increase in NO_3^- at PZII. Similarly, the annual average K, PO_4^{3-} and NH_4^+ concentrations were 2.08, 1.99, and 0.02 mg L^{-1} at PZI for groundwater, 3m from the stream. For PZII, the annual average concentrations for K, PO_4^{3-}, and NH_4^+ were 1.36, 1.98, and 0.03 mg L^{-1}, indicating similar trends relative to PZI. For groundwater concentrations adjacent to the stream, PZI was 1.70, 2.30, and 0.03 mg L^{-1} for K, PO_4^{3-} and NH_4^+, respectively, indicating a net decrease in K and a net increase in PO_4^{3-} and NH_4^+ from the riparian zone toward the stream. Similarly, for groundwater concentrations adjacent to the stream, PZII contained 1.54, 2.12, and 0.05 mg L^{-1} for K, PO_4^{3-}, and NH_4^+ respectively, indicating a net increase in K, PO_4^{3-}, and NH_4^+ across the riparian zone toward the stream. From the aforementioned results, the riparian zone located upstream (PZI) retained K, but displayed an increase in the NO_3^-, PO_4^{3-}, and NH_4^+ concentrations. The PZII site contained increasing concentrations of K, PO_4^{3-}, and NH_4^+, but the net amount of NO_3^- was not impacted. The results further indicate that shallow groundwater need not always attenuate NO_3^- nor be below a certain concentration level, as also noted by Hill (1996); and that the position of the riparian zone in relation to groundwater flow patterns and surface-subsurface interactions is critically important in forested ecosystems to prevent excessive nutrient loading in streams.

The mean shallow groundwater nutrient concentration was calculated for PZI and PZII (Table 3.2. and Figure 3.5.). Results indicated no statistical difference ($P \leq 0.05$) in NO_3^- concentrations between shallow groundwater sites. However, the observed maximum NO_3^- concentration was higher at PZII (0.20 mg L^{-1}) relative to PZI (0.12 mg L^{-1}) indicating potential seasonal variations in nutrient attenuation processes. The mean PZI groundwater PO_4^{3-} and K concentration was higher than that measured at PZII, whereas the NH_4^+ was higher at PZII relative to PZI (Table 3.2. and Figure 3.5.).

Based on seasonal variations (Table 3.3. and Figure 3.4.), the NO_3^- concentration was higher during late winter and early spring at PZI and PZII, after which the lower water residence time and increased plant uptake of NO_3^- is assumed to have resulted in the decrease in the NO_3^- concentration at both PZI and PZII, as shown by (Peterjohn and Correll, 1984; Hill, 1996). The PO_4^{3-} concentrations were higher during the fall at PZI and PZII when there was low plant uptake activity and when the depth to groundwater was greatest, further limiting plant activity. Additionally, total PO_4^{3-} concentrations in shallow groundwater steadily decreased to a minimum (0.03 mg L^{-1}) during summer when plant uptake of water and nutrients was higher at both sites. K and NH_4^+ displayed a reverse trend when summer had the highest concentrations of K and NH_4^+ at both PZI and PZII. The groundwater table was the lowest during the summer. The depth to groundwater was 176 and 161 cm at PZI and PZII, respectively, and plant water uptake activity was therefore assumed to be limited. At PZI, stream water predominantly infiltrated into shallow groundwater, which could explain the higher NO_3^- concentration in the piezometer closer to the stream (0.03 mg L^{-1}). However, due to the decrease in water residence time (due to lower interference from stream water intrusion) NO_3^- decreased to 0.01 mg L^{-1}. This characteristic was similarly noted in a review by Hill (1996) who reported on many studies (Lowrance *et al*., 1984; Peterjohn and Correll, 1984; Simmons *et al*., 1992) that provided evidence of higher NO_3^- concentrations in wells farthest from the stream.

At PZI and PZII water rapidly infiltrated 182 and 101 mm hr^{-1}, respectively (measured using double ring infiltrometers) presumably mixing with the shallow groundwater, and then flowed rapidly to the stream via highly conductive subsurface soils (hydraulic conductivity, Ks = 1.5 x 10^{-5} m s^{-1}), as reported in NLCD (2006) USDA soil maps by Fry *et al*. (2009). Since the depth to groundwater was low (approximately 144 cm), redox conditions at the subsurface were assumed spatially constant, resulting in the coexistence of mineralization, nitrification, plant uptake, and denitrification; thus leading to low and variable concentrations of ammonium and nitrate (McDowell *et al*., 1992). Results indicated that karst riparian geology may lower the NO_3^- concentration levels (0.01 mg L^{-1}) lower than that observed by Peterjohn and Correll (1984) who reported an NO_3^- value of 0.7 mg L^{-1}in a deciduous forest in Maryland, U.S., Lowrance *et al*. (1984) who reported an NO_3^- value of 0.44 mg L^{-1}in a deciduous forest in Georgia, U.S., Lowrance (1992) who reported an NO_3^- value of 0.8 mg L^{-1}in a pine and deciduous forest in Georgia, U.S., and Simmons *et al*. (1992) who reported an NO_3^- value of 1.6 mg L^{-1}in a deciduous forest in Rhode Island, U.S. Lower NO_3^- concentration levels at our study sites could be attributed to high water infiltration rates and subsequent NO_3^- leaching, dilution and transport through runoff (Hill, 1996; Levia *et al*., 2011).

Jordan *et al*. (1993) and Burt *et al*. (2010) suggested the presence of considerable uncertainty in quantifying exact nutrient removal rates by riparian vegetation. In a review of studies that focused on nitrate removal by riparian zones, Hill (1996) indicated that most authors could only provide empirical evidence of NO_3^- removal but could not provide estimations of NO_3^- removal due to vegetation uptake, as it was difficult to measure. Seasonal variations in SW and GW nutrient concentrations can be attributed to the change in the position of the water table, which will in turn change the soil moisture content, and thus result in change of nutrient leaching, weathering and denitrification rates (Hill, 1996; Burt *et al*., 2010, Levia *et al*., 2011). According to Hill (1996), most studies attributed an apparent increase in nutrient concentrations during storm events to the flushing of nutrients from subsurface soils, or alternatively that GW travel time towards the stream is reduced as the high flow in stream will force surface water into the subsurface soils, which subsequently reduces NO_3^- depletion in the GW.

In the current study, the hydrological connectivity between SW and GW systems and rapid infiltration and movement of water in the karst subsurface indicate that plant uptake of nutrients is minimal relative to that which is transported into surface water from shallow groundwater, as noted by Hoffman *et al*. (2006), Cirmo and McDonnell (1997), Lowrance *et al*. (1984), Peterjohn and Correll (1984). Hoffman *et al*. (2006) showed that a riparian ecotone in the River Gjern catchment, Jutland, Denmark had a 59 to 68% groundwater discharge and low nitrate and total phosphorus, relative to stream water nutrients. This finding was attributed to increased denitrification due to rapid shallow groundwater movement that results in increased soil moisture content and denitrification. Peterjohn and Correll (1984) conducted a study in the Rhode River drainage basin Maryland, indicating that 75% of total nitrate in the riparian forest was lost due to subsurface flow and that 61% of the SW nitrate concentration was attributable to GW discharge to the stream. Additionally, they reported that 41% of total phosphorus was lost to deep groundwater flow and the remaining 59% was lost due to subsurface flow. Lowrance *et al*. (1984), indicated that the nutrient sink nature of a riparian forest due to the fact that the GW contributed to only 1% of the total SW flow, and that most of GW was lost to deeper aquifers in Little River watershed . In the current study, the finding of lower GW nutrient levels, relative to SW concentrations, was in agreement with previous studies (Hoffman *et al*., 2006; Cirmo and McDonnell, 1997; Lowrance *et al*., 1984;

Peterjohn and Correll, 1984; Haycock and Pinay, 1993). However, even though riparian zone nutrient uptake, nutrient transformations and nutrient storage can reduce GW nutrient levels, the residence time of surface water or groundwater in the subsurface would not be enough to facilitate those processes in BREA and hence it is assumed that nutrients are lost to geochemical processes (Ford and Williams, 2007; Levia *et al*., 2011; Mahler *et al*., 2008). As confirmed by Hoffman *et al*. (2006), since the position of the bedrock (within 3m) and groundwater table is near the soil surface, denitrification and volatilization of nutrients were assumed dominant factors, relative to plant uptake and storage. Additionally, the presence of a clayey layer, 3 m below the ground surface (Fry *et al*., 2009), may restrict vertical shallow groundwater flow. The fact that the SW NO_3^- was greater than that of GW is consistent with the findings of Lowrance *et al*. (1984), Hill (1996), Jordan *et al*. (1993) who indicated that NO_3^- depletion may be a result of conversion to reduced nitrogen fractions, which were not quantified in this study.

3.4.3.3. Stream nutrient concentration variation with stream discharge

Hydrological controls on nutrient concentrations were analyzed using an inspection of the shape of hyperbolic curves (concentration verses discharge), and the strength of the parameter C_δ from Eq (3). Strong relationships between stream discharge and stream water nutrient concentration was observed for all nutrients (NO_3^-, K, and NH_4^+) except total P. Both NO_3^- and K exhibited dilution behavior (i.e. a decreasing concentration with an increase in discharge). Potassium had a stronger dilution relationship to discharge ($C_\delta = 1.5$) relative to NO_3^- ($C_\delta = 0.2$). Ammonium had a concentration effect with C_δ = -34.3. Total P was considered to be hydrologically constant with a low C_δ = 0.02 (Johnson *et al*., 1969; Barco *et al*., 2012; Stelzer and Likens, 2006; Salmon *et al*., 2001).

Observed nitrate results were similar to those of Barco *et al*. (2012) who identified a negative C_δ for NO_3^- at the Whippany River Watershed (located in Morris, NJ) and the Saddle River Watershed (in Bergen, NJ) indicating dilution behavior. Since the current study used four sampling points (SI to SIV) as input data for the hyperbolic model (Johnson *et al*., 1969), uncertainty in the hyperbolic model results was greatly reduced (Barco *et al*., 2012). Total PO_4^3 remained hydrologically constant and exhibited negligible seasonal variation, indicating that weathering in the watershed was limited and reflecting no external application of P. The increase in K with discharge (usually during the wet seasons, as shown in Figure 3.3.) could be attributed to an increase in weathering from parent materials and leaching from the soil solution (Burt *et al*., 2010; Barco *et al*., 2012). Additionally, as indicated by Salmon *et al*. (2001), increase in concentration of K with discharge could be due to weak biochemical cycling mechanisms that result in leaching of K with increase in discharge. Hence, it seems reasonable to infer that the geochemical processes, governed by rapid movement of water in karst geology, are more dominant in cycling and transforming SW-GW nutrients than biochemical processes (for example plant uptake), in this Ozark border forest ecosystem.

Chemographs of the dynamics of SW nutrients, in response to precipitation, indicated some similar trends to GW nutrients responses to storms (Figure 3.4.). Concentration changes, over the scale of hours to days, were assumed to be a result of nutrient transport to the stream from shallow groundwater. As per Hill (1996), Lowrance *et al*.(1984) and Peterjohn and Correll (1984), increases in stream nutrient concentrations during storm events could be due to an initial flush of nutrients from GW and soil surface through runoff and leaching of nutrients from the saturated soils (Barco *et al*., 2012).

3.4.4. Future Directions

Future research should consider nutrient concentration variations for a longer time series (i.e. year to year basis) to characterize the predominant nutrient cycling pathways. Nutrient budgets should be established that characterize individual nutrient cycling processes (especially plant nutrient uptake and denitrification in the riparian zone) (Lowrance *et al*., 1984; Burt *et al*., 2010). The relationships between biogeochemical cycling rates in the riparian zone, increased nutrient loading, and climate change is deserving of investigation, particularly in karst hydrogeological settings where hydrological flow regimes can be distinct. This is particularly important in low order streams where the most intensive interactions between terrestrial and stream ecosystems often occur (Hill, 2000). Global climate change may further influence nutrient concentration levels in the stream and shallow groundwater. Therefore, long-term studies are warranted (Hill, 2000).

Future investigations should include numerical physical process based models, such as MODFLOW and HYDRUS, as well as hydrology and nutrient data for predicting water quality and quantity at the BREA. Calibrated and validated models can then be used with fewer input data, for example climate data, in order to estimate nutrient loading in karst and other hydrogeological ecosystems with complex rapid shallow GW movement. Results from such physical process based models can aid as management tools for land managers wishing to predict the outcomes of future management scenarios (Jones and Mulholland, 2000).

3.5. Summary and Conclusions

High-frequency SW-GW nutrient concentration monitoring was conducted in a second-growth Ozark hardwood forest. Relative to the 5-year average, climate during the study period was cooler by 0.5 °C and drier by 30%. Annual average stream flow was greater at downstream locations, due to increasing GW input and increasing stream length reflecting a net gaining stream. Stream flow downstream, at sites SII and SIV, was 44 and 218% greater than that at SI and SIII respectively. Annual average stream water NO_3^- concentration decreased at downstream locations by 21, 38 and 38% at SII, SIII and SIV respectively, relative to stream water nitrate measured at SI (0.53 mg L^{-1}). Similarly, annual average stream water total PO_4^{3-} concentration decreased at downstream locations, by 15, 31 and 46% at SII, SIII and SIV respectively, relative to that at SI (0.13 mg L^{-1}). Annual average K for stream water increased at SII and SIII by 15 and 1% relative to that measured at SI (3.29 mg L^{-1}). Annual average stream water NH_4^+ for downstream locations varied minimally relative to SI. NH_4^+ changed negligibly, 0.01 and 0.02 mg L^{-1}, relative to that measured at SI (0.06 mg L^{-1}). Shallow groundwater nutrient concentrations were not significantly different ($p > 0.05$) between the two sites (PZI and PZII). Annual shallow groundwater NO_3^- concentration was the same (0.01 mg L^{-1}) at PZI and PZII, while total PO_4^{3-} increased by 33% at PZII (downstream) relative to

PZI (0.03 mg L^{-1}). Similarly, annual average shallow groundwater NH_4^+ concentration was greater at PZII by 100% relative to PZI (0.03 mg L^{-1}). Annual average shallow groundwater K concentration decreased at PZII by 22% relative to that at PZI (1.86 mg L^{-1}). Spatial and seasonal variations in stream water nutrient concentrations varied significantly ($p < 0.01$). Shallow groundwater nutrient concentrations were not significantly different between sites ($p > 0.05$), however, seasonal variations in nutrient concentration levels were significant ($p < 0.01$). Hyperbolic dilution model results indicated that both NO_3^- and K exhibited dilution behavior with increasing discharge, while NH_4^+ exhibited concentration behavior and total PO_4^3 was hydrologically constant.

This work showed that shallow groundwater nutrient cycling processes in karst hydrogeological systems may reduce nitrate loading. The seasonal variation of in-stream processes had a limited effect on in-stream NO_3^- concentrations (Royer *et al*., 2004). Therefore, the biogeochemical processes that cause NO_3^- lowering primarily occur within the riparian zone (Ranalli, 2010), and thus substantiate the current work's interest in quantifying the spatiotemporal variations in nutrient concentrations in this distinct ecosystem. As compared to other studies conducted in the U.S. (review in Hill, 1996), results from the current study showed lower shallow groundwater NO_3^- concentration levels in the summer. Higher NO_3^- levels were observed during winter, while lower levels were recorded in summer, suggesting that the NO_3^- trend was similar to many northern flowing streams (Mulholland, 1992). At the BREA, low NO_3^- rates were observed during plant growth seasons that could be attributed to increased plant uptake in the summer (Jones and Mulholland, 2000). NH_4^+, total PO_4^{3-}, and K exhibited lower concentrations in shallow groundwater relative to stream water concentrations. The increase in

NH_4^+concentration with an increase in discharge could be attributed to enhanced parent material leaching of NH_4^+ due to rapid water drainage in a karst geologic setting. This is an important conclusion that illustrates the complex nature of biogeochemical processes occurring in karst geology and the need for continued investigation. The baseline information accumulated from this research is invaluable for the implementation and improvement of physical process based predictive models that can accurately quantify outcomes of management scenarios on riparian zone groundwater quality and quantity.

3.6. Acknowledgements

Funding was provided by the Environmental Protection Agency [EPA] Region 7 [Grant Number: CD-97701401-0]. Results presented may not reflect the views of the EPA and no official endorsement should be inferred. Gratitude is extended to multiple members of the Interdisciplinary Hydrology Lab of the University of Missouri, School of Natural Resources. Sincere gratitude is extended to Stephen Pallardy and Kevin Hosman for climate data and valuable information about the BREA, and multiple reviewers whose comments improved the quality of the manuscript.

3.7. References

Barcelona, M. J., Wehrmann, H., Schock, M.R., Sievers, M., Karny J., 1989. Sampling frequency for ground-water quality monitoring. EPA report.

Barco, J., Gunawan, S., Hogue, T.S., 2012. Seasonal controls on stream chemical export across diverse coastal watersheds in the USA, Hydrol. Process., doi: 10.1002/hyp.9294

Beale, E., 1962. Some uses of computers in operational research, Industrielle Organisation, 31, 27-28.

Belden, A. C., Pallardy, S.G., (2009. Successional trends and apparent Acer saccharum regeneration failure in an oak-hickory forest in central Missouri, USA, Plant Ecol., 204, 305-322, doi: 10.1007/s11258-009-9593-4.

Bencala, K. E., 1984. Interactions of solutes and streambed sediment: 2. A dynamic analysis of coupled hydrologic and chemical processes that determine solute transport, Water Resour. Res., 20, 1804-1814.

Burgin, A. J., Hamilton, S.K., 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways, Front. Ecol. Environ., 5, 89-96.

Burt, T., Pinay, G., Sabater, S., 2010. What do we still need to know about the ecohydrology of riparian zones?, Ecohydrology, 3, 373-377, doi: 10.1002/eco.140.

Cassidy, R., Jordan, P., 2011. Limitations of instantaneous water quality sampling in surface-water catchments: Comparison with near-continuous phosphorus time-series data, J. Hydrol, 405, 182-193, doi: 10.1016/j.jhydrol.2011.05.020

Chinnasamy, P., Hubbart, J.A., (in submission). Measuring and Modeling Shallow Groundwater and Flow Connectivity to a Forested Ozark Border Stream, Earth Interact.

Cirmo, C. P., McDonnell, J.J., 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review, J. Hydrol., 199, 88-120, doi: 10.1016/S0022-1694(96)03286-6.

Critchfield, H. J., 1966. General climatology. Prentice-Hall, Englewood Cliffs, New Jersey.

Dahm, C. N., Grimm, N.B., Marmonier, P., Valett, H.M., Vervier, P., 1998. Nutrient dynamics at the interface between surface waters and groundwaters, *Freshw. Biol.*, 40, 427-451, doi: 10.1046/j.1365-2427.1998.00367.

Dottori, F., Martina, M.L.V., Todini, E., 2009. A Dynamic Rating Curve Approach to Indirect Discharge Measurement. Hydrol. Earth Sys. Sci., 13, 847-863.

Ensign, S. H., Doyle, M.W., 2006. Nutrient spiraling in streams and river networks, J. Geophys. Res., 111, G04009, doi: 10.1029/2005JG000114.

Ford, D. C., Williams, P., 2007. Karst hydrogeology and geomorphology, Second ed., John Wiley and Sons, New Jersey, USA.

Fry, J.A., Coan, M.J., Homer, C.G., Meyer, D.K., Wickham, J.D., 2009. Completion of the National Land Cover Database (NLCD) 1992–2001 Land Cover Change Retrofit product: U.S. Geological Survey Open-File Report 2008–1379, 18.

Gu, L., Meyers, T., Pallardy, S.G., Hanson, P.J., Yang, B., Heuer, M., Hosman, K.P., Liu, Q., Riggs, J.S., Sluss, D., 2007. Influences of biomass heat and biochemical energy storages on the land surface fluxes and radiative temperature, J. Geophys. Res., 112, 1-11, doi: 10.1029/2006JD007425.

HACH., 2007. DR 2800 Spectrophotometer Procedures Manual, HACH companies.

Haycock, N., Pinay G., 1993. Groundwater nitrate dynamics in grass and poplar vegetated riparian buffer strips during the winter, J. Environ. Qual., 22, 273-278.

Hill, A. R., 1996. Nitrate removal in stream riparian zones, J. Environ. Qual., 25, 743-755.

Hill, A.R., 2000. Stream Chemistry and Riparian Zones, in Jones, J.J., and Mulholland, P.J. (Eds.), Streams and Ground waters, Elsevier Publishing Co, San Diego, CA.

Hoffmann, C. C., Berg, P., Dahl, M., Larsen, S.E., Andersen, H.E., Andersen, B., 2006. Groundwater flow and transport of nutrients through a riparian meadow–Field data and modelling, Journal of Hydrology, 331, 315-335.

Johnson, N. M., Likens, G.E., Bormann, F., Fisher, D., Pierce, R., 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire, Water Res. Res., 5, 1353-1363.

Jordan, T. E., Correll, D.L., Weller, D.E., 1993. Nutrient interception by a riparian forest receiving inputs from adjacent cropland, J. Environ. Qual., 22, 467-473.

Kirchner, J. W., Feng, X., Neal, C., Robson, A.J., 2004. The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrol. Process., 18, 1353-1359.

Kulasova, A., Smith, P., Beven, K., Blazkova, S., Hlavacek, J., 2012. A method of computing uncertain nitrogen and phosphorus loads in a small stream from an agricultural catchment using continuous monitoring data, J. Hydrol., 458-459, 1-8

Likens, G. E., Bormann, F.H., Pierce, R.S., Eaton, J.S., Johnson, N.M., 1977. Biogeochemistry of a forested ecosystem, Springer-Verlag, New York, 146.

Lowrance, R., Todd, R., Fail, J., Hendrickson, Jr. O., Leonard, Jr. R., Asmussen, L., 1984. Riparian forests as nutrient filters in agricultural watersheds, BioScience., 374-377.

Mahler, B., Valdes, D., Musgrove, M., Massei, N., 2008. Nutrient dynamics as indicators of karst processes: Comparison of the Chalk aquifer (Normandy, France) and the Edwards aquifer (Texas, USA), J.Cont. Hydrol., 98, 36-49.

Marzolf, E. R., Mulholland, P.J., Steinman, A.D., 1994. Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams, Can. J. Fish. Aquat. Sci., 51, 1591-1599, doi: 10.1139/f94-158.

Mayer, P. M., Reynolds, S.K., Canfield, T.J., McCutchen, M.D., 2005. Riparian buffer width, vegetative cover, and nitrogen removal effectiveness: A review of current science and regulations Rep., US Environmental Protection Agency.

McClain, M. E., Richey, J.E., Pimentel, T.P., 1994. Groundwater nitrogen dynamics at the terrestrial-lotic interface of a small catchment in the Central Amazon Basin, Biogeochemistry., 27, 113-127.

McDowell, W. H., Bowden, W.B., Asbury, C.E., 1992. Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: subsurface solute patterns, Biogeochemistry., 18, 53-75.
Mulholland, P. J., 1992. Regulation of nutrient concentrations in a temperate forest stream: roles of upland, riparian, and instream processes, Limnol. Oceanogr., 37, 1512-1526.
Mulholland, P. J., Webster, J.R., 2010. Nutrient dynamics in streams and the role of J-NABS, J. N. Am. Benthol. Soc., 29, 100-117, doi: 10.1899/08-035.1
Niyogi, D. K., Bandeff, J.M., Selman, C., Menke, D.E., 2010. Nutrient flux, uptake, and transformation in a spring-fed stream in the Missouri Ozarks, USA, Aquat. Sci., 72, 203-212.
Ocampo, C. J., M. Sivapalan, C. Oldham., 2007. Hydrological connectivity of upland-riparian zones in agricultural catchments: Implications for runoff generation and nitrate transport, Journal of Hydrology, 331, 643-658, doi: 10.1016/j.jhydrol.2006.06.010.
Pallardy, S., Nigh, T., Garrett, H., 1988. Changes in forest composition in central Missouri: 1968-1982, Am. Midl. Nat., 120, 380-390.
Peterjohn, W. T., Correll, D.L., 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest, Ecology, 65, 1466-1475.
Pretty, J., Hildrew, A., Trimmer, M., 2006. Nutrient dynamics in relation to surface–subsurface hydrological exchange in a groundwater fed chalk stream, Journal of Hydrology, 330(1), 84-100.
Ranalli, A. J., Macalady, D.L., 2010. The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds–A review of the scientific literature, J. Hydrol., 389, 406-415, doi: 10.1016/j.jhydrol.2010.05.045
Richards, R. P., 2000. Estimation of pollutant loads in rivers and streams: A guidance document for NPS programs, Project report prepared under Grant X, 998397, 108.
Rochow, J. J., 1972. A vegetational description of a mid-Missouri forest using gradient analysis techniques, Am. Midl. Nat., 377-396.
Royer, T. V., David, M.B., Tank, J.L., 2004. Transport and fate of nitrate in headwater agricultural streams in Illinois, J. Environ. Qual., 33, 1296-1304.
Salmon, C. D., Walter, M.T., Hedin, L.O., Brown, M.G., 2001. Hydrological controls on chemical export from an undisturbed old-growth Chilean forest, J. Hydrol, 253, 69-80.
Simmons, R. C., Gold, A.J., Groffman, P.M., 1992. Nitrate dynamics in riparian forests: microbial studies, J. Environ. Qual., 21, 666-671.
Stelzer, R. S., Likens, G.E., 2006. Effects of sampling frequency on estimates of dissolved silica export by streams: The role of hydrological variability and concentration-discharge relationships, Water. Resour. Res., 42, W07415, doi:10.1029/2005WR004615.
Strahler, A., 1952. Hypsometric (area-altitude) analysis of erosional topography, Bull.Geol. Soc. Am, 63, 1117-1142.
United States Environmental Protection Agency., 2000. Water Quality Standards for Surface Waters. http://water.epa.gov/scitech/swguidance/standards/index.cfm.

Vidon, P., Allan, C., Burns, D., Duval, T.P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., Sebestyen, S., 2010. Hot Spots and Hot Moments in Riparian Zones: Potential for Improved Water Quality Management1, J. Am. Water Resour. As., 46, 278-298, doi: 10.1111/j.1752-1688.2010.00420

Wang, Y. G., Kuhnert, P., Henderson, B., 2011. Load estimation with uncertainties from opportunistic sampling data–A semiparametric approach, J. Hydrol., 396, 148-157, doi: 10.1016/j.jhydrol.2010.11.003.

Young, F. J., Radatz, C.A., Marshall, C.A., 2003. Soil Survey of Boone County, Missouri Natural Resources Conservation Service, 25 – 35.

CHAPTER IV: MODELING HYDROLOGIC AND NUTRIENT RELATIONSHIPS BETWEEN SURFACE WATER – SHALLOW GROUNDWATER IN AN OZARK BORDER STREAM USING MODFLOW

4.0. Abstract

Studies of stream water (SW) – shallow groundwater (GW) interactions are limited in the central U.S. Despite there being many models that simulate SW-GW interactions, few studies have used models to improve mechanistic understanding of SW-GW interactions in karst hydrogeologic systems. The numerical model–MODFLOW was coupled with the nutrient transport model-MT3DMS to simulate hydrologic and nutrient flux between a second order stream and the shallow aquifer in the riparian zone of a second growth Ozark border forest for the 2011 water year. MODPATH was used to delineate hydrologically active SW-GW interaction zones and to estimate spatiotemporal variations in flowpath length and travel time. Models were run in transient state to quantify seasonal and monthly variations in SW-GW hydrologic and nutrient interactions. Shallow GW modeling with MODFLOW provided numerical approximations of hydrologic and nutrient flux, that are comparable to observations of

SW-GW hydrologic and nutrient data (NS =0.47, r^2 =0.77, RMSE =0.61 cm and MD =0.46 cm). Annual average model estimations indicated that for more than 82% of the reach length, the shallow aquifer was recharged by stream water, while the remaining 18% of the stream length was recharged by water influx from the shallow aquifer. MT3DMS results showed that the shallow aquifer had the highest nitrate loading during the winter season (707 Kg d^{-1}). Particle tracking simulations revealed significant spatial variations between sites PZI-PZII (p =0.089) in subsurface flowpath and travel time in the study area, ranging from 213 m and 3.6 years to 197 m and 11.6 years. This study emphasizes the significance of karst geology in regulating SW-GW hydrologic and nutrient interactions and provides baseline information that will improve future management plans.

4.1. Introduction

In recent years interest in surface water (SW) - shallow groundwater (GW) interactions has increased dramatically. The increased interest is largely attributable to the realization that surface water and groundwater are not isolated components of the hydrologic regime but are instead integrated watershed processes (e.g. climate, geology, and surface topology) that include many biological factors (e.g. aquatic and riparian zone primary productivity) (Hynes, 1975; Sophocleous, 2002; Burt *et al*., 2010; Jones and Mulholland, 2000). Sophocleous (2002) and Woessner (2000) reviewed current studies explaining that effective management of water resources requires improved understanding of SW-GW interactions. Scientists have identified that rescaling the traditional view of streams to include the riparian zone will increase interdisciplinary opportunities for expanding the knowledge of hydrogeologic processes, leading to improved management of stream and floodplain ecosystems (Woessner, 2000).

Multiple physical processes influence SW-GW interactions. The dominant physical process for a given region depends on the climate, the geology, and the topography of the region (Jones and Mulholland, 2000; Levia *et al*., 2011; Burt *et al*., 2010). For example, in a region with highly conductive riparian soils, water enters GW within the riparian zone mainly as a result of drainage from adjacent hillslopes via recharge from deeper confined aquifers (Swanson and Wondzell, 1996), or by advected surface water (Jones and Mulholland, 2000). Hydraulic gradients between GW and SW, and the hydraulic gradients of streambed and subsurface soil are controllers of SW-GW interactions with dominant surface water advection (Fetter, 1994; Jones and Mulholland, 2000). Given that many processes control SW-GW interactions, elucidating the lateral extent, volume, and the residence time of SW-GW hydrologic fluxes will greatly improve understanding of the importance of SW-GW interactions in stream ecosystem processes and therefore management of associated natural resources (Kashara and Wondzell, 2003; Levia *et al*., 2011; Jones and Mulholland, 2000).

Accurate spatial and temporal representations of surface water – groundwater (SW-GW) interactions are critical for understanding stream nutrient loading from the adjacent riparian zone. Considerable research has shown that riparian zone shallow groundwater often has a lower nitrate concentration as compared to that in surface water (Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985; Haycock and Pinay, 1993; Jordan *et al*., 1993; Lowrance *et al*., 1995; Hill, 1996; Cey *et al*., 1999; Clement *et al*., 2003; Lee *et al*., 2000). Increased denitrification rates in GW, relative to SW, has been reported as the major reason for low GW nitrate concentration levels (Jacobs and Gilliam, 1985; Ambus and Lowrance, 1991; Addy *et al*., 1999). Such, increases in the denitrification rate are primarily due to processes that raise the soil moisture content and water storage in the riparian soil. Since SW-GW hydrologic interactions can increase the groundwater table during periods of elevated stream flow, it is necessary to quantify spatial and temporal variations in net water flow from the stream to the subsurface using groundwater flow paths within the riparian zone to better understand and predict of SW-GW nutrient relationships to the flow regime.

To overcome field-based methodological limitations (e.g. in-stream tracer tests, instrumentation requirements) groundwater models are increasingly used to characterize SW-GW interactions (Jones and Mulholland, 2000; Schilling *et al*., 2004; Wroblicky *et al*. 1998; Storey *et al*. 2003; Gooseff *et al*. 2003; Kasahara and Wondzell 2003;

Sophocleous, 2002; Woessner, 2000). Groundwater flow models range from simple index based models to complex physical process based models. In recent years many studies (Wroblicky *et al*. 1998; Woessner 2000; Storey *et al*. 2003; Gooseff *et al*. 2003; Kasahara and Wondzell 2003;) have used numerical simulation models (e.g. MODFLOW, CPFLOW, SUTRA, HYDRUS) in order to understand SW-GW interactions in varying hydrogeologic settings. According to Hunt and Feinstein (2012), MODFLOW (McDonald and Harbaugh, 1988) is one of the most widely used shallow groundwater models.

MODFLOW was first released in 1984 (Harbaugh and McDonald, 1996a and 1996b; Harbaugh *et al*., 2000; Hunt and Feinstein., 2012). Harrington *et al*. (1999) used MODFLOW to show that lateral flow rates ranged from 4 – 38 m yr^{-1} (average 19.4 m yr^{-1}) and 0.4 – 5.5 m yr^{-1} (average 1.9 m yr^{-1}) in two south Australian Otway basins - the Gambier unconfined and the Dilwyn confined system, respectively. Wroblicky *et al*. (1998) simulated the lateral extent of SW-GW interactions within the riparian zone and hydrologic flux rates through the riparian zone along two first order stream channels in Aspen Creek and Rio Calveras (New Mexico, U.S) and found that the hydraulic conductivity of alluvium and the variation in recharge rates had the greatest impact on the magnitude, the direction, and the spatial distribution of SW-GW interactions. The aforementioned studies showed MODFLOW’s potential for simulating SW-GW interactions and variations in flowpaths in varying geologic settings. Kasahara and Wondzell (2003) estimated SW-GW hydrologic fluxes and residence times along a mountain stream in the Cascades and found that the channel morphology features strongly controlled SW-GW flow and the residence time of water in the subsurface.

Wondzell and Swanson (1996) used MODFLOW to analyze the seasonal and storm dynamics of the SW-GW water flux and reported that the subsurface flux was 79% of the stream discharge at summer low flow, 2% during winter baseflow, and 0.7% during storms, indicating the potential for MODFLOW to provide accurate estimates of temporal trends in SW-GW interactions. In addition to simulating ground-water flow, in recent years, the utility of MODFLOW has been expanded to include solute transport and particle tracking (Harbaugh *et al*., 2000). In a study conducted in the Netherlands, Hefting *et al*. (2006) used MODFLOW to quantify nitrate loading in the shallow groundwater of a riparian zone and reported that nitrate loads were high within the forested zone, 87 g NO_3^- m^{-2} y^{-1}, relative to a grassland riparian zone, 15 g NO_3^- m^{-2} y^{-1}. These authors showed the potential of MODFLOW to estimate nutrient transport, as well as the ability of the model to estimate SW-GW interactions justifying the models use to quantify spatiotemporal variations of SW-GW hydrologic and nutrient concentration flux.

Despite the growing interest in SW-GW interactions (Sophocleous, 2002) and the availability of effective groundwater modeling tools, SW-GW research in the central U.S. has been limited. In particular, SW-GW interactions in Ozark border karst forested regions of mid-Missouri are not well characterized. There is therefore a great need for baseline SW-GW flow and nutrient data that will a) supply a basis for future best management practices and b) predict possible outcomes of future management scenarios. The following work investigates the potential of MODFLOW to improve operational decision-making in stream reaches influenced by SW-GW interactions in Ozark border forested regions of the central U.S. during water year (WY) 2011. The primary objectives of this study were as follows: (1) to assess the ability of MODFLOW 2000 to accurately predict shallow aquifer transient hydraulic head distribution in a kart system; (2) to quantify spatiotemporal variations in SW-GW hydrologic exchange; (3) to quantify the seasonal nitrogen flux between surface and shallow groundwater; and (4) to identify the spatial extent for which SW-GW interactions are active in the riparian zone.

4.2. Methods

4.2.1. Study site

This study took place in the University of Missouri Thomas S. Baskett Wildlife Research and Education Area (BREA, Rochow, 1972) located in the Ozark border region of south-central Missouri, U.S. (Pallardy *et al*., 1988). The BREA is a 2nd growth mixed deciduous forest and has not been subject to major natural or anthropogenic disturbances in the past 60 years. Research was conducted on two reaches of Brushy Creek within the BREA (Figure 4.1.). Brushy Creek is a second order stream (Strahler, 1952) with an average slope of 0.94% and joins Cedar creek, 4 km south of the BREA, after draining a watershed with an area of 9.17 km^2.

The BREA has a humid - continental climate (Critchfield, 1966). Mean January and July temperatures are -2.2 °C and 25.4 °C, respectively, while mean annual precipitation is 1,037 mm, as recorded between the years 1971 and 2010 at the Columbia Regional Airport, 8 km north of the BREA. The average annual temperature, from 2005-2010, measured at the on-site Ameriflux tower, was 13 °C; and average precipitation was 930 mm versus 12.9 °C, and 1,089 mm at the Columbia Regional Airport during the same time period. The underlying geology of BREA is of an Ordovician and Mississippian age. Dominant soils are Weller silt loam and Clinkenbeard clay loam (Rochow, 1972). Riparian soils consist of Cedargap and Dameron soil complexes (USDA soil map unit 66017). The BREA soils are well drained with average bulk density of 1.2 to 1.4 g cm^{-3} (Young *et al*., 2001). Riparian soils can be divided into three major layers with a silty surface layer (extending from 0 to 38 cm), a silt loam textured second layer (from 38 to 78 cm), and a gravelly third layer (from 78 to 150 cm). Depth to bedrock in the riparian zone is approximately 150 cm (USDA, 2009). The BREA's current land use ranges from second growth forests in the southern portion to pastures in the northern portion. The watershed consists of 2.6% suburban land use, 17.9% cropland, 33% grassland, 43.2% forest, and 3.3% open water and wetlands (USDA, 2009). The BREA's vegetation consists of northern and southern division oak-hickory forest species (Rochow, 1972) including American Sycamore (*Platanus occidentalis*), American Elm (*Ulmus americana*), and Black Maple (*Acer nigrum*) dominated riparian reaches (Belden and Pallardy, 2009). Understory vegetation consists of sugar maple (*Acer saccharum*), flowering dogwood (*Cornus florida*), and black cherry (*Prunus serotina*) (Reed, 2010).

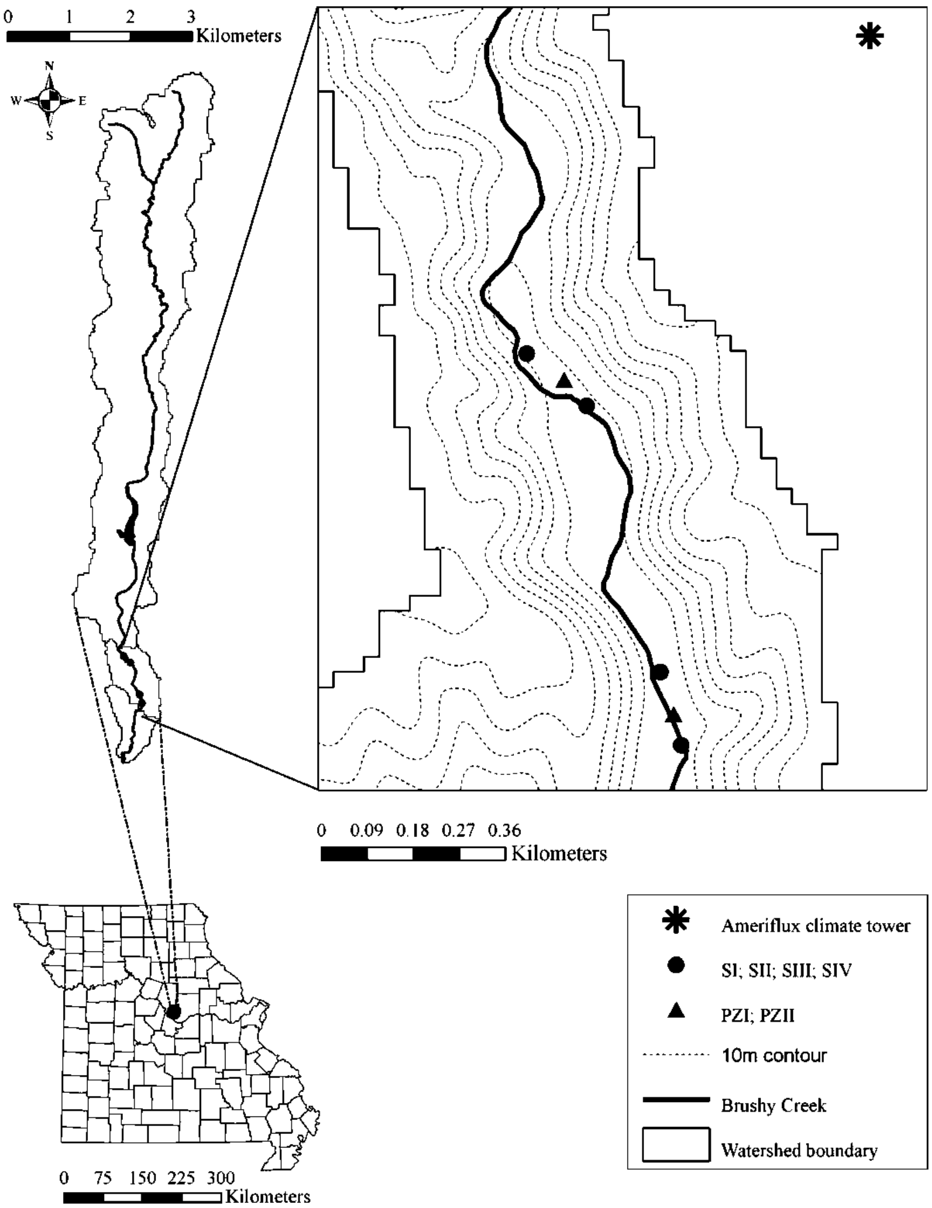

Figure 4.1. Study sites and instrument locations at Baskett Wildlife Research and Education Area, central Missouri, U.S. *S* represents stilling well site and *PZ* represents piezometer site.

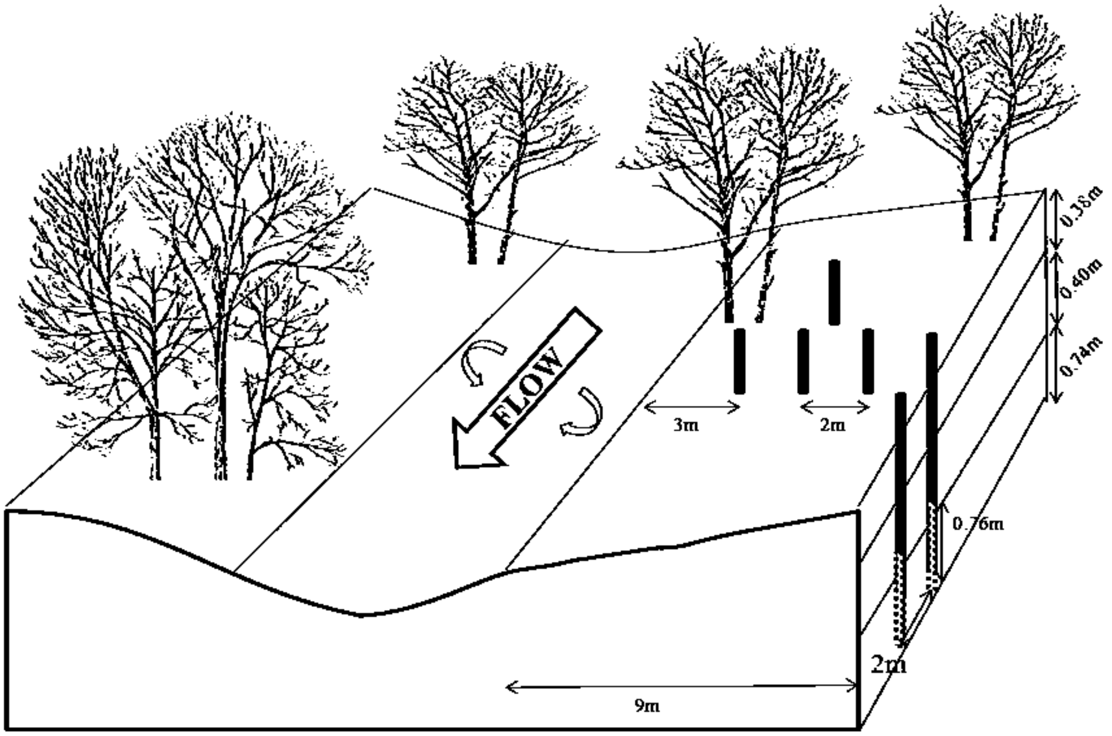

Figure 4.2. Conceptual diagram showing cross-section of piezometer study design at Baskett Wildlife Research and Education Area, central Missouri, U.S.

4.2.2. Instrumentation and data description

4.2.2.1. Climate data

Meteorological data were collected from an AmeriFlux tower, located at an elevation of 238 m, on a forested ridge approximately 100 m outside of the watershed (Figure 4.1.). Flux tower data were available via public ftp server (ftp://ftp.atdd.noaa.gov/pub/GEWEX/2010/mo/). Precipitation (Campbell Scientific Inc., TE525 Texas Electronics rain gauge, with an error of ± 1% for rates up to 2.54 cm hr^{-1}) and air temperature data (Vaisala HMP45C-L temperature sensor, with an error of ± 0.2 °C from 0 °C to 60 °C; and ± 0.4 °C at -35 °C) were downloaded for the 2011 WY.

4.2.2.2. Stream stage and hydraulic head measurements

Four in-stream stilling wells were installed (hereafter referred to as SI – SIV) during April 2010 in order to estimate stream discharge entering and leaving each study reach (Figure 4.1.). Stilling wells were equipped with a Solinst® Levelogger Gold pressure transducer (with an error of ± 0.003 m) with the stream stage recorded at five minute intervals. Streamflow rating curves were determined from measured stage-discharge relationships using the stream cross section method (Dottori *et al*., 2009) with a Marsh-McBirney ® Flo-Mate flow meter (with an error of ± 2%) to measure the stream velocity.

Between SI and SII, six piezometers were installed in transect (Piezometer Site I hereafter referred to as PZI) extending 3 m from the stream edge to 9 m into the riparian zone (Figure 4.1.). PZI was located at an elevation of 177 m along an east-west stream reach approximately 90 m long and 15 m wide at the bankfull. Similarly, Piezometer Site II (PZII) was located between SIII and SIV, at an elevation of 174 m, along an approximate north-south stream reach 157 m long and 10 m wide at bankfull. Each 3.58 m drive-point piezometer had a 4 cm inner diameter and a 76 cm slotted screen at the end (Figure 4.2.), and was equipped with a Solinst® Levelogger Gold pressure transducer that recorded hydraulic head at five minute intervals. To compensate for elevation differences between wells care was taken to adjust the water level in each well to incorporate elevation differences from the datum by adding gravitational head (calculated from the difference in depth of wells from a reference datum).

4.2.3. Numerical Modeling

4.2.3.1. Model description and assumptions

Shallow groundwater flow was modeled using MODFLOW 2000 (McDonald and Harbaugh, 1984), a three dimensional finite difference model, distributed with a graphical user interface by Aquaveo (Groundwater Modeling System -GMS). Solute transport and the lateral extent of surface water-groundwater interactions were modeled using the MODFLOW extensions MT3DMS and MODPATH. MODFLOW 2000 was preferred over MODFLOW 2005 given that MODFLOW 2000 is the more widely used version, with proven success in varying geologic settings. Unlike MODFLOW-2000, MODFLOW-2005 does not include a parameter-estimation process (Harbaugh, 2005), which might be useful for transferability of current work (e.g. to estimate hydraulic conductivity values if the model is applied to another study site).

The ground surface elevation assigned to the model layers was obtained from the 5 m 2007 Missouri Spatial Data Information Service (MSDIS) Digital Elevation Model (DEM). The model area was 1227 x 3855 m, with the eastern, western, and southern boundaries defined by Brushy Creek watershed boundaries and the northern boundary following the groundwater flow line defined by the elevation at that point. The initial grid spacing across the model domain was 10 x 10 m and was later refined to 2 x 4 m, which was the smallest cell size feasible, constrained by computing power.

Natural Resources Conservation Service and USDA soil maps (USDA, 2009) were used to identify the three dominant soil layers of each study site. Therefore, the model consisted of three-layer, regular block-centered, finite difference grids with a 0.1

m cell length. The bottom layer was 0.74 m thick, with hydraulic conductivities of 86.4 and 8.64 m d^{-1} for Kx, Ky, and Kz, respectively. The hydraulic conductivity (K) was estimated using ROSETTA, a built-in computer program in HYDRUS – 1D (Schaap *et al.*, 2001) that estimates pedotransfer functions (PTFs) by supplying the textural class and two groundwater head values as input data (Schaap *et al*., 1998). The bottom layer had a gravel texture and 44.6%, 32.6%, and 22.8% of sand, silt, and clay, respectively. Kz was set an order of magnitude lower in order to reflect the anisotropy commonly observed in such systems as per USDA (2009) and Storey *et al*. (2003). The second layer, with a silt loam texture and 24.4%, 57.4%, and 18.2% of sand, silt, and clay, respectively, was 0.46 m thick with three dimensional hydraulic conductivities of 0.18 (Kx and Ky) and 0.018 m d^{-1} (Kz). The top layer, an alluvium deposit with a silt loam texture and 18.3%, 63.1%, and 18.6% of sand, silt and clay, respectively, was 0.38 m thick with hydraulic conductivities of 8.64 and 0.864 m d^{-1} for Kx, Ky, and Kz, respectively. The assigned K values were validated with slug tests performed on site (see Calibration and Validation) and with the values mentioned in Freeze and Cherry (1979). For layers one to three, soil porosity was set to 0.4, 0.5, and 0.3, respectively, as per the values published in Anderson and Woessner (1992). Similarly, the specific yield and the specific storage were 0.2, 0.09, 0.3 m^{-1}, and 1 $x10^{-4}$, 1 $x10^{-3}$, and 1 $x10^{-5}$ (Fetter, 2001; Anderson and Woessner, 1992; Freeze and Cherry, 1979) for layers one to three, respectively.

Brushy Creek was represented by a specific head arc with nodes representing the observed daily stream stage. The elevation of the stream was quantified by DEM (5 m resolution). Observed daily precipitation data were used to define the recharge per day and was applied as a constant recharge flux to the top of the most active layer. The bottom of the third layer (gravel) was assigned a no-flow boundary condition due to presence of confining layer and/or bedrock (USDA soil maps, 2009). However, as inferred from steady state simulations, the model boundaries were allowed to permit regional groundwater flow. The model was initially run at steady state, following which the model parameters (specifically, Kx, Ky, and Kz, the width and the depth of the stream, the alluvial layer, and the model solver package) were each parameterized independently. In particular, K values were parameterized according to the range specified in Freeze and Cherry (1979) and the pedotransfer functions.

4.2.3.2. Model calibration and validation

As per methods used by Storey *et al*. (2003), the MODFLOW model was run at steady state, and specific parameters (Kx, Ky, and Kz, the alluvial layer, time step and the model solver package) were systematically altered to best reflect conditions of Brushy Creek Watershed as listed in the USDA (2009) soil maps. Model simulated observation wells (n = 12) were placed at piezometer locations in order to compare modeled data with observed data. MODFLOW was calibrated for a period of three months (April to June, 2010 with a total of 91 time periods). During the calibration period, soil physical and hydrological (specifically Kx, Ky, Kz, specific storage, porosity, longitudinal dispersivity, and specific yield) parameters were adjusted as per the methods of Swanson and Wondzell (1996), Latuz and Seigel. (2006) and Schilling *et al*. (2006). During the calibration period, the estimated error interval was set to $\pm$ 0.01 m, with a confidence interval of 95%. The residual (difference between observed and modeled head) was calculated in order to assess the performance of the model. Thus, following calibration, a residual near zero was achieved and the model was validated from July to September, 2010.

To quantify model bias, observed and modeled head values were evaluated using the Nash-Sutcliffe Efficiency parameter (NS) (Nash and Sutcliffe, 1970), the Root Mean Square Error (RMSE) (Willmott, 1981), the Mean Difference (MD) (as used by Swain *et al*. 2004) and the standard regression method (r^2). NS parameter values range from -∞ to 1.0 where 1.0 indicates that the model is in perfect agreement (Moriasi *et al*. 2007; Luo and Sophocleous, 2010). RMSE values closer to zero indicate better model performance (Moriasi *et al*. 2007). The equation of the best-fit regression line (the coefficient of determination) can indicate the agreement between the modeled and observed head provided that the modeled and observed heads vary linearly (Luo and Sophocleous, 2010). The equations needed to calculate the aforementioned statistics are, as follows:

$$NS = \frac{voN - \sum_{i=1}^{N}(x_i - yi)^2}{voN} = 1 - \frac{\sum_{i=1}^{N}(x_i - yi)^2}{\sum_{i=1}^{N}(x_i - \bar{x})^2} \qquad [1]$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(x_i - yi)^2}{N}} \qquad [2]$$

$$MD = \frac{1}{N}\sum_{i=1}^{N}(x_i - yi)^2 \qquad [3]$$

where *vo* is the variance of observed values, N is the number of data points, *xi* is the observed value, *yi* is the corresponding predicted value, and $\bar{x}$ is the average observed value for the study period.

Researchers have used a variety of time series to study SW-GW interactions. While many studies used long time series (i.e. more than three years) recent studies have shown that, a short time series (from several months to one year) is sufficient to study dominant processes in SW-GW interactions. For example, using a ten-day simulation and one day calibration, Lautz and Siegel (2006) used MODFLOW and MT3D to show that the movement of SW into GW was predominantly an advective process at Red Canon Creek of the Rocky mountains. Schilling *et al*. (2006) used MODFLOW and MT3DMS for a four month study period (with three day calibration) to evaluate dilution and denitrification process in riparian zone groundwater at Walnut Creek in Iowa. Swanson and Wondzell (1996) used MODFLOW to quantify SW-GW hydrologic fluxes, during storm events for a one year study period (eight day calibration), in a 4^{th} order mountain stream at McRae Creek in H.J. Andrews Experimental Forest in Oregon. They concluded that SW-GW flow rates were positively correlated to stream flow during base-flow conditions, but decrease during storm events due to high infiltration rates in the riparian zone. Given the successful outcomes of the aforementioned studies that identified key processes influencing SW-GW hydrologic and nutrient interactions, the use of high-frequency (weekly) short-term (one year) hydrologic and nutrient data (Barcelona *et al*.,

1989) to quantify spatiotemporal variations in SW-GW nutrient interactions is a strength of the current work.

4.2.3.3. Groundwater flow modeling

Model parameters used in this study are listed in Table 4.1. Once calibrated, the model was executed in steady state mode to estimate the starting heads. The hydraulic heads at each cell were then used as initial heads for transient simulations. A more detailed discussion of the parameterization of the MODFLOW code is contained in the MODFLOW User's Manual (Harbaugh *et al*., 2000).

The model was then implemented with piezometer transects, with the well screen open at the third soil layer. The cells for which daily hydraulic heads were known (i.e. cells overlapping the stream and the piezometers) were isolated and the head data was entered. Daily stream hydraulic head values (n=4 sites, Figures 4.1. and 4.2.) were input into the model. MODFLOW estimates the head values at other locations along the stream by interpolation (McDonald and Harbaugh, 1984). Hydraulic head values for the start and end point of the stream were assigned to the elevation of the stream at that point as per Anderson and Woessener (1992).

Table 4.1. Model parameter values used in MODFLOW.

Model Parameters	Layer 1 (silt)	Layer 2 (silt loam)	Layer 3 (gravel)
Horizontal grid size (m)	2 x 4	2 x 4	2 x 4
Layer thickness (m)	0.38	0.46	0.74
Hydraulic conductivity Kx (m d^{-1})	8.64	0.18	86.4
Horizontal Anisotropy	1	3	1
Vertical Anisotropy	10	10	10
Specific Yield (m^{-1})	0.2	0.09	0.3
Specific Storage	1×10^{-4}	1×10^{-3}	4×10^{-5}
Longitudinal Dispersivity αl(m)	3.048	1.524	6.096
Horizontal/Longitudinal Dispersivity αh/αl	1	1	1
Vertical/Longitudinal Dispersivity αv/αl	0.5	0.5	0.5
Porosity	0.4	0.5	0.3

4.2.3.4. Nitrate transport modeling

Groundwater flow results obtained from the MODFLOW simulation were used as inputs to the Modular 3-Dimensional Transport Multi Species (MT3DMS) model (Zheng and Wang, 1999). Active cells in the MT3DMS transport model were identical to those in the flow model. The stilling well locations (SI to SIV) and the piezometer locations were set as specific concentration nodes. Weekly nitrate concentration data (mg L^{-1}) for WY 2011 (n=52) collected at stream stage monitoring sites SI to SIV, and in riparian zone shallow groundwater wells (Chinnasamy and Hubbart, in submission), were used as specific concentration boundary conditions for the model. The external sources and sinks of nitrate loading in the aquifer were primarily from the stream. The nitrate concentration along the study reach was interpolated by the model using available nitrate concentration data at the stilling well locations (Figure 4.2.). Since the study area was within a conservation area and within a second growth forest, it was assumed there were negligible nitrate inputs from external sources (such as drainage, leakage, and fertilizer applications). The MT3DMS model was then run at daily time steps with MODFLOW in order to assess spatiotemporal variations in aquifer nitrate loading (kg m^{-2}) for the entire WY 2011. A more detailed discussion of the concepts and the fundamental ideas behind the MT3DMS module can be found in the MT3DMS user's manual (Zheng and Wang, 1999).

4.2.3.5. Surface water – groundwater lateral interaction extent modeling

MODPATH was forced with groundwater flow results from MODFLOW. MODPATH is a particle tracking post-processing module for computing the lateral extent of SW – GW interactions and flowpaths (Pollock, 1994). MODPATH also computes the travel times associated with each particle. MODPATH particles, which are imaginary water particles (Pollock, 1994), were placed upstream of SI and SIII (stream gauging locations) in order to compute the lateral extent of the flowpaths that begin in the stream, pass through the shallow aquifer, and then rejoin the stream. Monthly variations in flowpaths were assessed by running MODPATH along with monthly MODFLOW results. A more detailed discussion of the fundamental processes of the MODPATH module can be found in MODPATH's user's manual (Pollock, 1994). As shown in a study by Storey *et al*. (2003), stream morphological characteristics such as meanders, woody debris, and the presence of boulders were omitted. Streambed heterogeneities and evapotranspiration that can affect net SW – GW flux volume (Woessner, 2000;

Sophocleous, 2002) were also beyond the scope of the current work, but provide impetus for future investigations.

4.3. Results and Discussion

4.3.1. Climate during the study period

Climate in the BREA during WY 2011 was characterized by mean air temperature of 12.5 ˚C and total precipitation of 647 mm. The maximum precipitation for a single day was 44 mm on December 31, 2010. Seasonal precipitation (winter, spring, summer, and fall) was 170 mm from December - March, 250 mm from March – June, 135 mm from June – September, and 94 mm from September to December. Annual precipitation during the water year was approximately 21% lower than the 30 year average (1971-2012) of 816 mm measured at the Columbia Airport (6 km from BREA). The annual mean air temperature was approximately 11% cooler relative to the 30 year average air temperature of 14.1˚C.

4.3.2. Hydraulic heads in the monitoring wells

Observed 5-min interval hydraulic heads at the four stilling wells (SI to SIV) and the 12 piezometers (Pz1 to Pz12) were averaged to daily values for WY 2011 (Figure 4.3.). During WY 2011, SI had the highest average stage (178.36 m) followed by SIII, SIV, and SII with 178.56, 178.49, and 177.03 m, respectively (Table 4.2.). The winter and spring seasons had a higher stage (average = 178.69 m) relative to the summer

(178.45 m) and fall (178.42 m). The difference in stage measurements at the streambed between the upstream (SI) and the downstream location (SIV at 830 m apart) was higher during fall (0.15 m) and summer (0.13 m) relative to winter (0.12 m) and spring (0.11 m). The stream flow followed the streambed's varying elevation differences, along the study reach, more closely during low flow conditions than during high flow conditions (as expected). Annual average daily groundwater head was higher at PZII (178.37 m) relative to PZI (177.18 m). Similar to the observed stage, the groundwater head was higher during the winter and spring (178.59 m at PZI), followed by summer (178.21 m at PZI) and fall (178.12 m at PZI). Average depth to groundwater was 69.70 cm at PZI and 92.32 cm at PZII during spring months (32% difference), and 253.41cm at PZI and 231.30 cm at PZII during fall months (8% difference). During the dry season (October – November with 8% difference between sites), depth to groundwater was 214.9 cm and 197.61 cm at PZI and PZII, respectively, and water level in the piezometers dropped below average level (126.62 and 150. 93 cm at PZI and PZII).

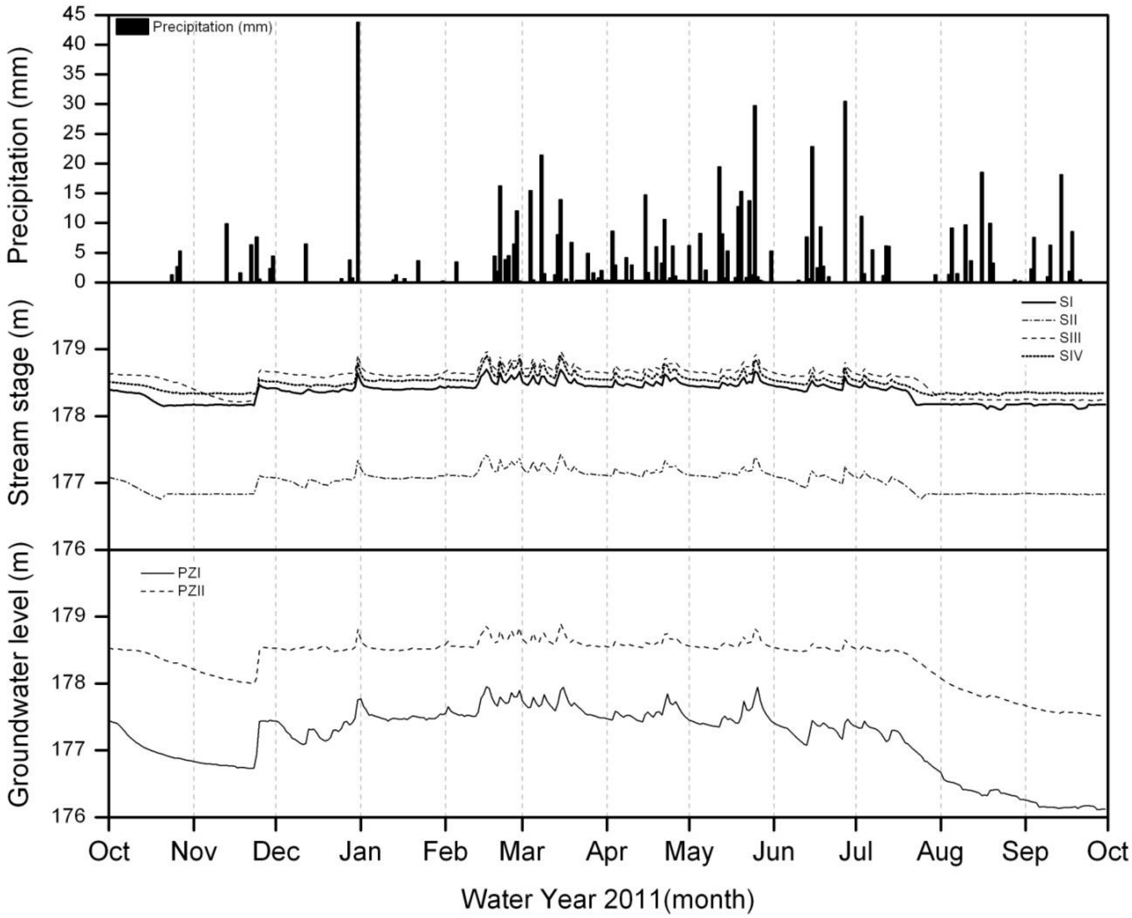

Figure 4.3. Measured precipitation (mm), hydraulic head at stream (m) and at piezometer (m) locations during WY 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

Table 4.2. Descriptive statistics of hydraulic heads and error analysis between observed and modeled heads Baskett Wildlife Research and Education Area, central Missouri, U.S.

Location	Observed Head (m)				Error Analysis Parameter			
	Mean	Std. Dev.	Maximum	Minimum	NS	RMSE (m)	MD (m)	r^2
Stream Stage								
SI	178.36	0.14	178.70	178.10	-	-	-	-
SII	177.03	0.15	177.44	176.76	-	-	-	-
SIII	178.56	0.19	178.98	178.21	-	-	-	-
SIV	178.50	0.13	178.91	178.31	-	-	-	-
PZI	177.18	0.49	177.95	176.12	-	-	-	-
PZII	178.37	0.34	178.89	177.51	-	-	-	-
Shallow Groundwater Level								
Pz1	177.22	0.48	177.98	176.18	-0.14	0.51	-0.35	0.64
Pz2	177.20	0.48	177.97	176.13	-0.21	0.53	-0.38	0.54
Pz3	177.22	0.47	177.99	176.23	-0.26	0.53	-0.38	0.65
Pz4	177.18	0.49	177.97	175.99	-0.28	0.56	-0.40	0.60
Pz5	177.13	0.49	177.91	176.02	-0.54	0.61	-0.46	0.55
Pz6	177.12	0.51	177.94	176.01	-0.41	0.60	-0.14	0.57
Pz7	178.30	0.34	178.78	177.43	0.08	0.33	-0.23	0.74
Pz8	178.35	0.34	178.85	177.49	0.25	0.29	-0.19	0.77
Pz9	178.39	0.33	178.88	177.52	0.39	0.26	-0.14	0.74
Pz10	178.45	0.35	179.05	177.58	0.47	0.25	-0.08	0.76
Pz11	178.38	0.34	178.90	177.53	0.32	0.28	-0.16	0.75
Pz12	178.35	0.34	178.88	177.50	0.23	0.30	-0.19	0.75

4.3.3. Model calibration and validation

Model calibration was completed as delineated in the Methods. After a residual of 0.001 and 0.000 m was achieved at PZI and PZII, respectively, the model parameters were saved and used for the validation period (July to September, 2010), from which the residual was 0.003 and 0.001 m at PZI and PZII, respectively. Nash-Sutcliffe values ranged from -0.54 to 0.47 (Table 4.2.). The best NS value of 0.47 was obtained at Pz10 (located in PZII) (Table1) located in the center of the model boundary. The RMSE values ranged from 0.25 to 0.61, while the MD and r^2 values ranged from -0.08 to 0.46 m, and

0.77 to 0.54, respectively. The average NS, RMSE, MD, and r^2 values at PZII were 0.29, 0.29 m, -0.17 m, and 0.75, respectively, and were better than the average NS, RMSE, MD and r^2 values of -0.31, 0.56 m, -0.35 m, and 0.59 at PZI, respectively. Therefore, relative to PZI, the MODFLOW hydraulic head predictions were closer to actual head values for the piezometers located at PZII (Figure 4.4.), which was located in the center of the modeling domain.

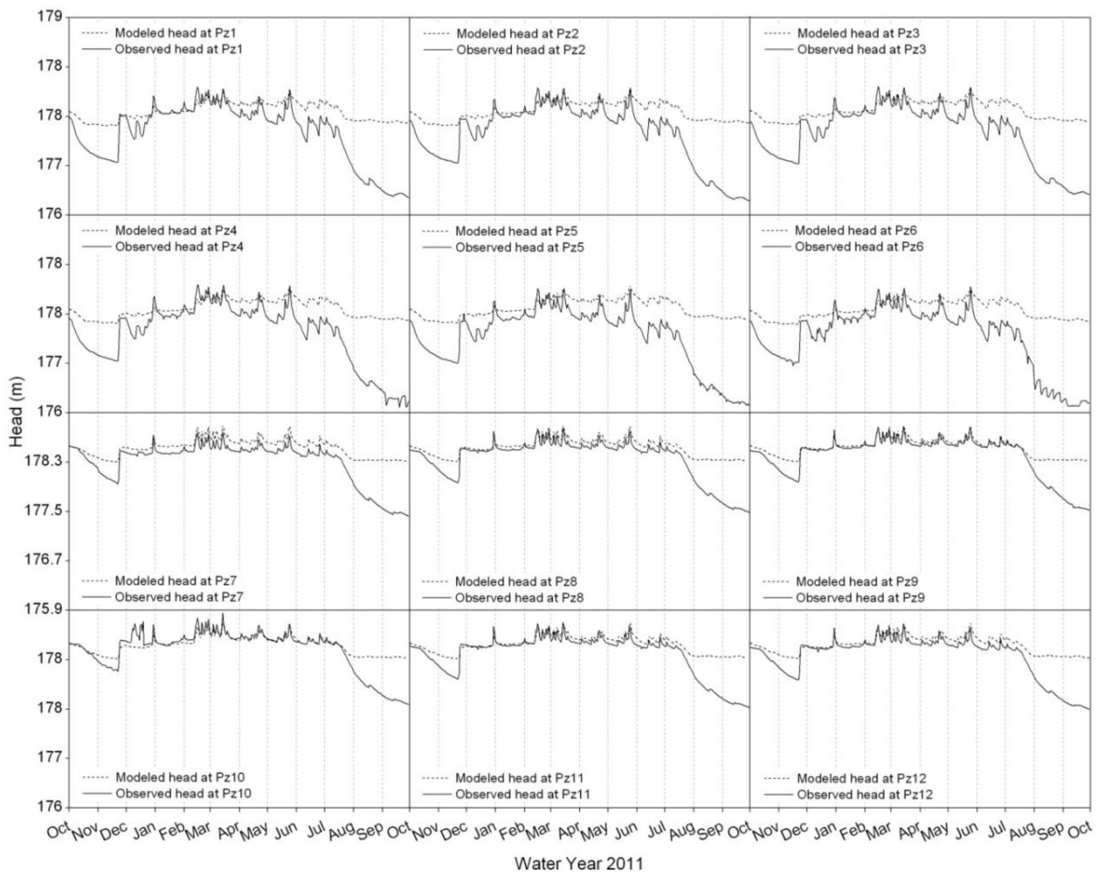

Figure 4.4. Observed versus modeled (MODFLOW) hydraulic heads for piezometers located at piezometer site PZI (Pz1 to Pz6) and at piezometer site PZII (Pz7 to Pz12) over WY 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

4.3.4. Groundwater flow simulations

Figure 4.5. illustrates variations in the water table contours generated by MODFLOW for November, February, May, and August of WY 2011. For WY 2011, the entire study reach was on average a losing system with 1,988 m^3 d^{-1} lost to GW. On an annual average, the study reach between SI and SII (160 m in length) was a losing reach (1,201m^3 d^{-1}); between SII and SIII (543 m in length) was also a losing reach (1,129 m^3 d^{-1}); and between SIII and SIV (149 m in length) was a gaining reach (343 m^3 d^{-1}). Thus, on average the study reach lost more water to the shallow aquifer during summer (2,405 m^3 d^{-1}) relative to water lost during the fall (2,184 m^3 d^{-1}), spring (2,102 m^3 d^{-1}), and winter (1,549 m^3 d^{-1}) seasons. This result is reasonable considering the majority of rainfall occurs from early to mid-summer months in central Missouri.

These results are similar to other studies in the central U.S. Marzolf *et al*. (1994) reported average stream flow gain of 17.28 m^3 d^{-1} in a study conducted at Walker Branch Creek (reach length = 62 m) in Tennessee (i.e. 0.9% of the stream flow gain observed at Brushy creek with reach length = 830 m). The higher flow in Brushy Creek relative to Walker Branch Creek study is explained in part by larger drainage area and study reach length. Mulholland *et al*. (2007), indicated that the Hugh White Creek (reach length = 78 m) in North Carolina was on average a gaining reach with GW input of 140 m^3 per day, which is 7% of the volume of water lost in Brushy Creek per day. Presumably, the presence of a karst geology in BREA could lead to greater SW water loss to the GW aquifer relative to the geology present at Walker Branch Creek and Hugh White Creek, indicating the importance of geology in SW-GW flow processes. At BREA, the study reach lost 2,331m^3 d^{-1} to the aquifer and gained 343 m^3 $d^{-1}$from the aquifer (annual average). Downstream of SIV, up to the end of the watershed, the water table contours gradually decreased, indicating that streamflow was gradually lost to the aquifer. Monthly plan view maps (Figure 4.5.) of water flow vectors indicated that shallow groundwater primarily flows along layer three (the gravel layer) due to a higher hydraulic conductivity relative to other layers. A visual inspection of flow vectors at every layer indicated that during higher streamflow periods a significant amount of water movement occurred from the stream toward the subsurface aquifer in the top and second layers.

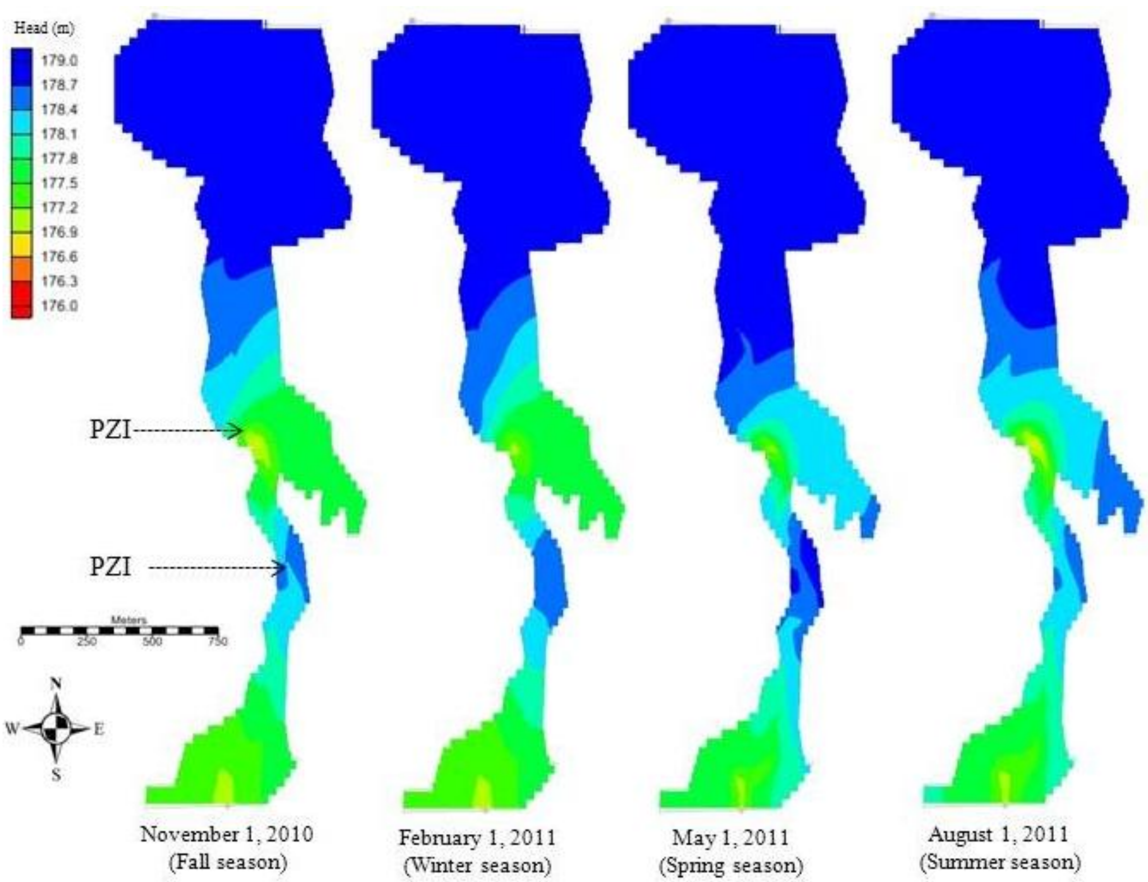

Figure 4.5. Plan view of MODFLOW estimates of hydraulic head distribution (m) for the months of November, February, May and August over the WY 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

4.3.5. Surface water – groundwater interactions

Model results indicated that the seasonal variation in stream discharge, aquifer recharge, and precipitation were the primary extrinsic forces driving surface – groundwater interactions, nitrate transport, and the lateral extent of SW-GW interactions. The MODFLOW flow budget results further indicated that flux rates at the stream reach alternated between positive, where water entered the aquifer (study reaches SI-SII, SII-SIII, and SI-SIV) and negative, where water entered the stream from the aquifer (study reach SIII-SIV). Alternating between a losing or gaining stream indicates that stream water lost to the aquifer may reemerge at downstream locations depending on the flowpath and residence time. This result is in agreement with previous research that indicated that shallow groundwater flow directions near the stream were highly spatially variable and bidirectional with shallow groundwater flowing both toward and away from the stream (e.g. Wondzell and Swanson, 1996; Marzolf *et al*. 1994; Fellows *et al*., 2001; Jones and Mulholland, 2000). The groundwater flux per unit stream reach length was similar for the three study reaches, with values of 2.08, 2.30, and 2.47 $m^3\ d^{-1}\ m^{-1}$ for reaches SII-SIII, SIII-SIV, and SI-SIV, respectively. This result indicates that the water flow per unit length of the stream did not change greatly in magnitude between stream reaches, and that the geomorphological and soil physical properties did not differ much between study reaches. Understanding variations in geomorphology along a stream reach is valuable information for land managers wishing to regulate SW-GW connectivity (Levia *et al*., 2011). The high groundwater flux rates observed at BREA indicate high SW-GW connectivity that can be attributed to karst geology and the presence of hardwood forest. Hardwood forest species use the water stored in the riparian zone for metabolic processes (i.e. transpiration), which provides an increased soil water gradient for flow and holding capacity (Hill, 1996). Mulholland *et al*. (1997) reported a groundwater flux rate of 1.80 m^3 d^{-1} m^{-1} at Hugh White Creek (reach length = 72 m), North Carolina, while Marzolf *et al*. (1994) and Fellows *et al*. (2001) reported groundwater flux rates of 0.80 and 0.04 m^3 d^{-1} m^{-1} at Walker Branch Creek (reach length = 62 m) in Tennessee and Rio Calaveras (reach length 110 m) in New Mexico respectively. These studies concluded that the lateral extent of SW-GW hydrological connectivity was proportional to the groundwater flux rate. The comparisons made above indicate that Brushy Creek could have a greater lateral SW-GW extent than that observed in other regions of the U.S., likely attributable to karst flowpaths.

4.3.6. Nitrate transport and loading

Temporal variations in nitrate concentrations between SW and GW were significant ($p < 0.01$) during the study period. Spatial variations between SW nutrient concentrations were also significant ($p = 0.001$). Groundwater nutrient concentrations however, were not significantly different ($p > 0.05$) between sites. Nitrate concentrations within the study reach were the highest during winter (0.994 mg L^{-1}), followed by the spring (0.346 mg L^{-1}), summer (0.200 mg L^{-1}), and fall (0.113 mg L^{-1}) seasons of WY 2011. The MT3DMS model results indicated a net annual nitrate loss of -328 Kg d^{-1} from the study reach (830 m) to the aquifer. Study reach SI to SII (distance 160 m) lost, on average 54 Kg d^{-1} to the aquifer, while SII to SIII (distance 543 m) lost 268 Kg d^{-1}, and SIII to SIV (distance149 m) lost 6 Kg d^{-1} to the aquifer. Nitrate loading to the aquifer increased with stream reach length (r^2 = 0.95, Figure 4.6.). Relative to other study reaches, the SIII-SIV reach had the lowest nitrate loading. This result could be attributable to the fact that the SIII-SIV reach length was the shortest relative to other study reaches, and that there was more water input from the shallow aquifer to the stream at SIII-SIV that may have diluted nitrate. Study reaches SI-SII and SII-SIII had the highest nitrate losses during the winter season (107 and 594 Kg d^{-1}, respectively), while SIII-SIV had the highest nitrate losses during spring (10 Kg d^{-1}). Study reaches SI-SII, SII-SIII, and SIII-SIV had the lowest nitrate losses during the fall season, with a net average loss of 13, 71, and 1 Kg d^{-1}, respectively (Figure 4.6.). MT3DMS results indicated a lateral extent of 70 m up to which surface-groundwater hydrologic and nutrient mixing occurred.

The daily average nitrate loading from the stream to the aquifer (328 Kg d^{-1}) was lower than the range in average amount of nitrate uptake by a second order stream (10,000 to 100,000 Kg d^{-1}), as reported by Ensign and Doyle (2006). Thus, nitrate loading was lower than the amount of nitrate that can be processed by a second order stream (Ensign and Doyle, 2006). This result implies that even though in-stream processes can reduce nitrate concentrations, nitrate is transported to the adjoining aquifer through water transport before in-stream nitrate loss can happen. The stream thus becomes a source of nitrogen to the shallow aquifer. The aquifer nitrate loading observed at different stream reach sites in Brushy Creek was significantly different ($p < 0.001$) indicating that the rate of in-stream nitrate cycling processes could be different between headstream locations and downstream locations (Ensign and Doyle, 2006). Therefore, management plans to regulate nutrient loading should differentiate between headwaters and downstream locations.

The current study results indicated that Ozark border streams, such as Brushy Creek, can be a source of nitrate to riparian zone aquifers during shallow groundwater recharge events. Peterjohn and Correll (1984) showed that a deciduous forest can have an average of 20, 50, 60 Kg ha^{-1} yr^{-1} of N from precipitation, upslope groundwater sources and leaf litter decomposition, respectively. Using Peterjohn and Correll's (1984) estimated rates for BREA, the N received from Brushy Creek surface water of 85.5 Kg ha^{-1} yr^{-1} indicates that a major proportion (40%) of the annual deciduous forest riparian zone nitrogen budget is received from surface water loading. The results also identifies that Brushy Creek serves as a N source to the riparian zone.

Denitrification and plant nutrient uptake rates can improve MODFLOW prediction; however, denitrification and plant uptake rates were not measured for the current work. Future nutrient flux work should focus on vegetation cover and the rate of the mobilization of soil nutrients to groundwater and the delivery to surface water. While not directly studied, it is assumed that the nitrate concentration was lowered (by more than 90%) in the riparian zone by biogeochemical processes (Levia *et al*., 2011). Future studies should focus on quantifying specific biogeochemical transform rates in the riparian zone (e.g. the nitrification and denitrification of nitrates and the volatilization of ammonium) thereby increasing understanding regarding hydrologically mediated biogeochemical processes in the Ozark border region of the central U.S.

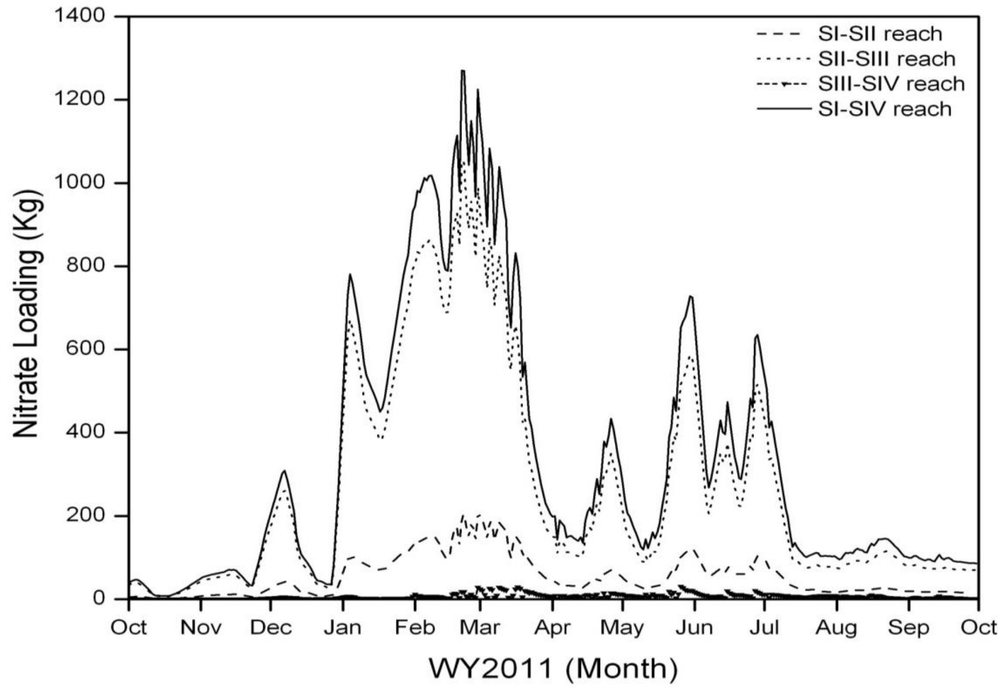

Figure 4.6. MT3DMS estimates of nitrate loading in the shallow aquifer from different segments of the study reach for the WY 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

4.3.7. Spatiotemporal variations in the lateral extent of surface water – groundwater interactions

MODPATH revealed significant spatiotemporal variations (Table 4.3. and Figures 4.7. and 4.8.), between sites PZI-PZII, ($p < 0.05$) in subsurface flowpath and travel time, ranging from 213 m and 3.6 years to 197 m and 11.6 years. The variations in lateral extent of SW-GW interaction length (10 to 50 m) indicate that forest managers should be sensitive to SW-GW connectivity that may stretch beyond current recommended buffer widths. The annual average flowpath distances at PZI and PZII were 196 and 189 m, respectively. The annual average travel time was 106% higher at PZII (4326 d) than at PZI (1330 d), indicating that the nutrients transported by water had more time to undergo nutrient biochemical transformations in the subsurface at PZII, relative to PZI. Extended residence times also indicate that water is stored longer in the soil matrix at PZII, and can therefore be available for plant uptake. The computed near stream flowpaths from Brushy Creek appeared, disappeared, contracted, and expanded in response to seasonal hydrologic changes (Figures 4.7. and 4.8.). Modeling results indicated identical behavior on the unmonitored side of the riparian zone. Therefore, management implications derived from the model can be applied to either side of the stream reach. During drier months (May in particular) flowpaths did not extend into the piezometer transect, but were restricted to the stream bank and within the stream channel (i.e. the hyporheic zone). During such periods, surface – groundwater interaction were negligible. These results indicate that even during low flow periods, the majority of the stream reach was losing to the GW and was therefore hydrologically well-connected. During no flow periods, SW-GW hydrologic connectivity could not be quantified in this work, as there were no wells present in the streambed.

The spatial extent of SW–GW interactions can increase biodiversity as it provides habitat for aquatic invertebrates and increases plant available water (Khashara and Wondzell, 2000). The baseline results from this study will provide a foundation for the development of future management plans that should include consideration of water residence time and storage in the riparian zone. Monthly MODPATH results indicated spatiotemporal variations in flowpath length and travel time and thus indicate that riparian zone management plans should consider seasonal dynamics in SW-GW lateral extents. In particular, increases in flowpath length results in lengthened in travel time. Therefore, water has greater residence time in shallow aquifers and therefore time to undergo biogeochemical reactions. Given annual average travel times at PZI and PZII of

3.6 (1,329 days) and 11.8 (4,326 days) years, respectively, annual average nutrient concentration at PZII (0.009 mg L^{-1}) was 18% lower than that in PZI (0.011 mg L^{-1}). In-stream nutrient processing could be the reason for the observed lower nutrient loading in the downstream extents (SIV) of Brushy Creek. Due to increased precipitation (80%) during the fall season, the model predicted increased flowpath lengths and corresponding increases in the travel time (Figures 4.7. and 4.8.).

MODPATH results indicated 37, 31, 3 and 37 distinct flowpath lines (Figure 4.7.) for November, February, May and August of WY 2011 respectively. The specific location of flowpath lines is important for management plans in terms of buffer strip planning (Bentrup, 2008). According to Pollock (1994), information about dominant subsurface flowpath lines that originate from the stream can be used to predict future stream meandering patterns. Wroblicky *et al* (1998) reported an annual average of nine and six distinct flowpath lines for study sites located at Aspen Creek and Rio Calaveras, in New Mexico, respectively. Seasonal variations were not reported. More distinct flowpath lines observed along Brushy Creek could be due to the presence of karst geology in the study area. The variability in the number of distinct flowpath lines during WY 2011 indicates that the stream reach alters between a losing and gaining system, as described in Wroblicky *et al*. (1998). Lautz and Siegel (2006) reported 17 distinct flowpath lines with varying lengths in Red Canyon Creek in Wyoming. They further reported that the residence time ranged from several hours to 10 years, relative to an average of 7 years observed at BREA. The average length of flowpath length at Red Canyon Creek was also shorter (150 m) relative to that at BREA (205 m). These comparisons indicate that water may travel faster and further in the subsurface karst geological layers at BREA, relative to Red Canyon Creek. The shorter average residence times at BREA, relative to that at Aspen Creek, Rio Calaveras and Red Canyon could be due to the relatively high hydraulic conductivity (i.e. karst geology) at BREA. The nutrients transported in the karst flowpath lines have shorter time to undergo biochemical cycling, relative to that found in other studies (e.g. Lautz and Siegel (2006). However, the nutrients can be lost to deeper aquifers or karst flowpaths below subsurface flowpaths (Hill, 1996) and hence management plans should investigate methods to increase plant nutrient uptake before they are lost to deep aquifers.

Table 4.3. Seasonal and spatial MODPATH lateral flowpath length and travel time results for study sites at Baskett Wildlife Research and Education Area, central Missouri, U.S.

WY 2011Month	Lateral Flowpath Length (m)		Travel Time (d)	
	PZI	PZII	PZI	PZII
October	209	89	1196	2633
November	211	104	1310	3751
December	264	75	2807	1835
January	211	86	1225	2437
February	209	77	1206	1870
March	209	105	1209	3695
April	207	103	1171	4202
May	208	104	1173	4007
June	208	105	1172	3834
July	209	825	1167	15355
August	207	351	1153	4288
September	209	346	1170	4009

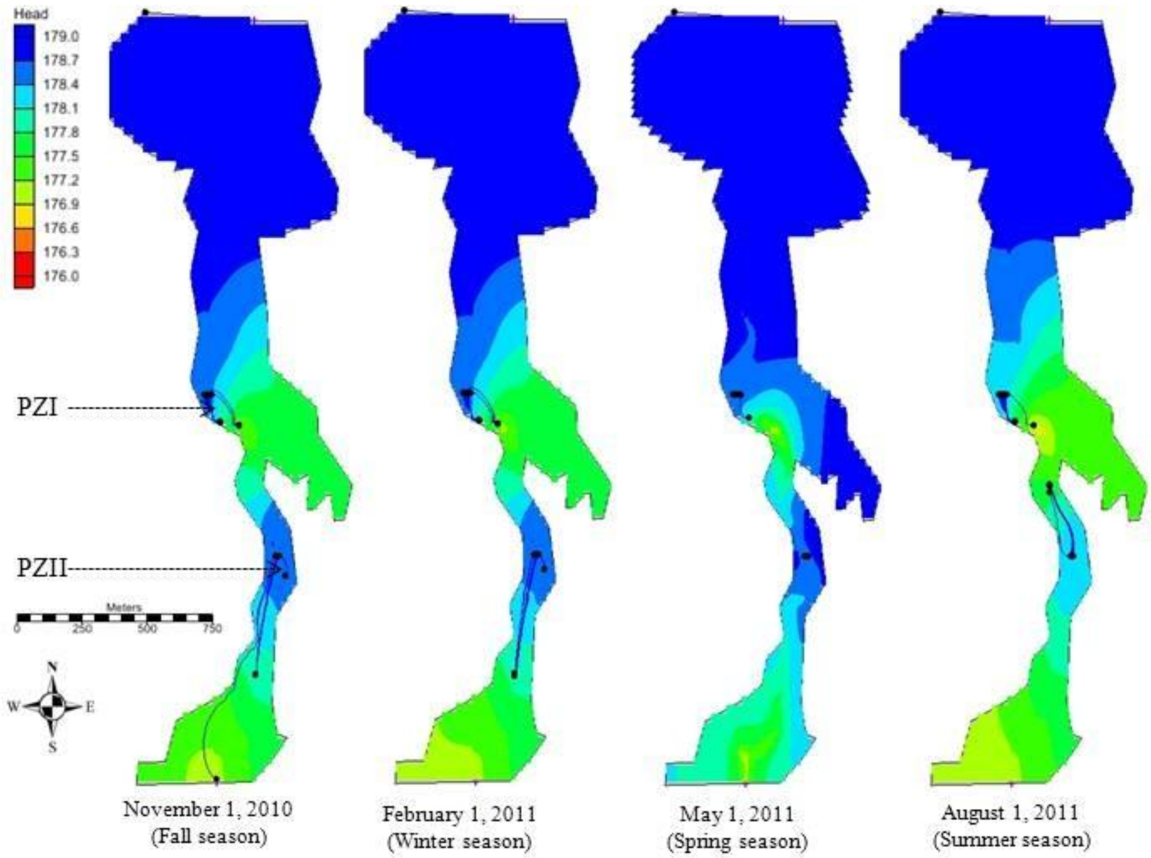

Figure 4.7. MODPATH estimates of lateral extent of surface water – groundwater interactions for the months of November, February, May and August over the WY 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S. The solid lines indicate flowpaths as simulated by MODPATH.

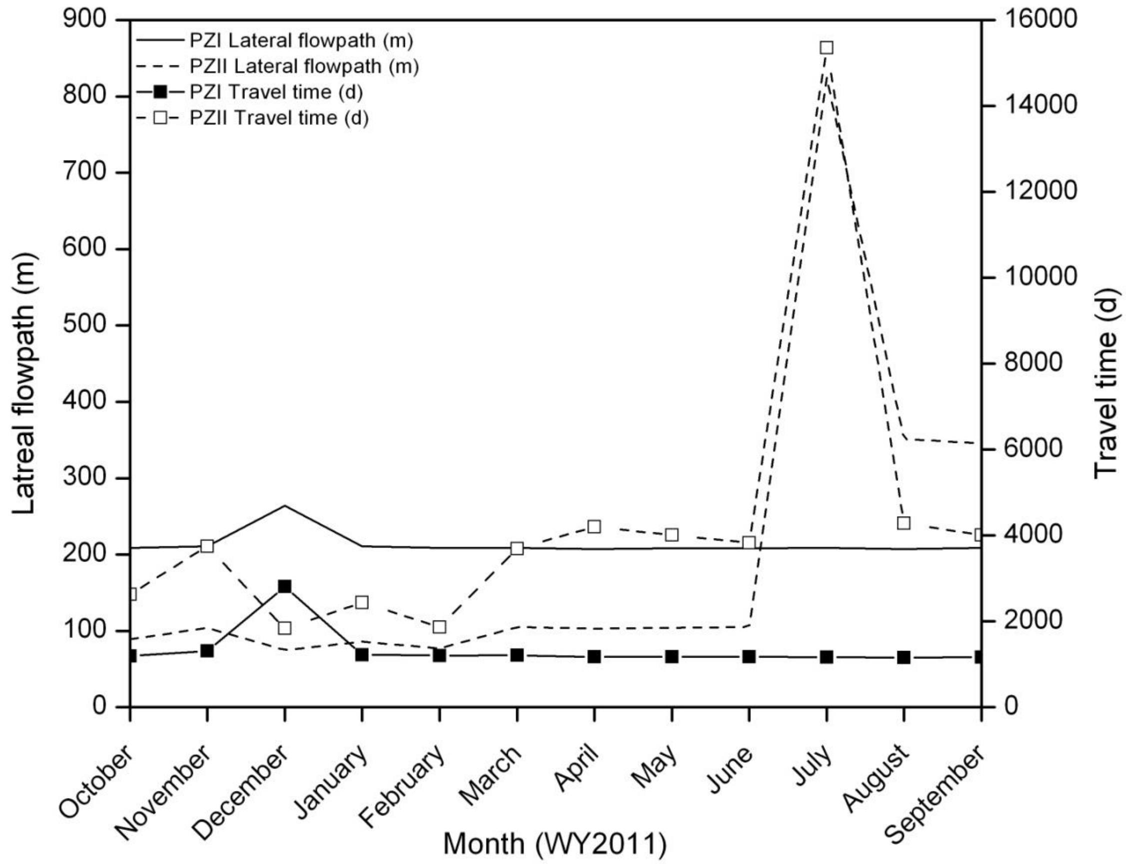

Figure 4.8. MODPATH estimates of lateral extent (m = meter) of surface water – groundwater interactions and travel time (d = day) of water in flow paths over the WY 2011 at Baskett Wildlife Research and Education Area, central Missouri, U.S.

4.3.8. Model Limitations

The accuracy of subsurface water flux estimates, which are proportional to the hydraulic conductivities ($K_{x,y,z}$), are limited to the accuracy of Ks (Swanson and Wondzell, 1996) which is difficult to measure and often limited to available information in the published literature (Freeze and Cherry, 1979; Jones and Mulholland, 2000, Fetter, 2001).

A finer model grid mesh size could aid in reducing errors between the observed and modeled head values. However, as previously indicated, due to limitations in computing power, the authors could not use finer mesh sizes. For example, using a mesh size resolution of 1m x 1m, for the current study area, a computer would need to have at least 500 GB of free hard disk space and 4GB of RAM cache memory.

The absence of borehole data, for quantifying the model stratigraphy, could also introduce simulation errors. Due to the absence of nitrate concentration data at the model boundaries, our study results were limited to the identification of nutrient loading within the aquifer from surface water to the last piezometer located nine meters from the streambank. Since the current study focused only on advection and dispersion processes in the cycling of nitrate, the biological processes that affect the nitrate-cycling rate (i.e. denitrification) were omitted. However, given the results from this investigation, the nutrient loading results at BREA can be primarily attributed to groundwater – surface water flow interactions.

4.4. Conclusions

In this work, surface water - groundwater hydrologic and nutrient interaction modeling using MODFLOW, MT3DMS and MODPATH was shown to be effective for determining spatiotemporal variations in magnitude and extent of SW-GW interactions in karst geology of the mid-west. The current study approach is novel with regard to the use of transient flow conditions (as opposed to steady state conditions) in underrepresented karst geology of the mid-west. Transient simulations were possible due to the availability of high-frequency water quality (weekly nutrient concentration data) and water quantity (stream and shallow groundwater flow) monitoring networks established at BREA.

MODFLOW results indicated that the study reach was on average a losing stream (82% of the length) with significant seasonal variations ($p < 0.05$). The shallow groundwater flux per unit length was 2.47 $m^3\ d^{-1}\ m^{-1}$ and was not significantly different ($p > 0.05$) between study sites. The MT3DMS model results indicated a net annual nitrate loss of -328 Kg d^{-1} from the study reach to the GW. However, even with a high nitrate loading, GW nitrate concentrations were low compared to that of SW. Results indicated high nitrate concentrations of surface water relative to groundwater (greater than 90%) over the study period. The study results indicated that most of the nitrate transport to the subsurface aquifer from the stream occurs because of advection processes (i.e. physical processes) that vary spatially and temporally. The stream also serves as a nitrate source to the riparian zone for 80% of the stream length. MODPATH revealed significant spatiotemporal variations, between sites PZI-PZII, ($p < 0.05$) in subsurface flowpath and travel time, ranging from 213 m and 3.6 years to 197 m and 11.6 years. The annual average travel time was 106% higher at PZII (4326 d) than at PZI (1330 d), indicating that the nutrients transported by water had more time to undergo biochemical transformation in the riparian zone subsurface at PZII, relative to PZI.

In this work, the use of MT3DMS along with MODPATH in MODFLOW has increased modeling confidence for estimating the lateral extent of SW-GW interactions (70 m) in karst geology of the mid-west. The lateral extent of SW-GW interaction was not uniformly distributed along the study reach, but exhibited temporal variations (i.e. disappeared, expanded, contracted, and (or) reappeared). Results from the current study are likely representative of flow regimes in similar geologic setting environments across the central U.S.

According to Enyart (2009), in the Missouri Woody Biomass Harvesting Best Management Practices Manual, a 15 m stream side management buffer width is recommended for the BREA. However, according to the current study's results, a variable riparian zone buffer width (as opposed to a constant buffer width for the entire watershed) will be more suitable to prevent excess nutrient loading in Brushy Creek at locations where the stream is gaining. At locations where the stream is losing (82% of the length), native plants with high nutrient uptake rates could be used to prevent excess GW nutrient loading by SW. As per Bentrup (2008), a wider and larger (greater than 15 m) is required at locations where SW nutrient loading is high and where the SW-GW mixing zone stretches beyond 15 m. Study results indicate that future streamside management plans could benefit by including field and modeling analysis.

The current work provides a clear example in which shallow aquifer fluctuations are controlled by the surface water hydrologic regime. The baseline data provided by this study can be used to improve management plan formulations and to improve model confidence in predicting management outcomes. Since understanding hydrologic processes is a prerequisite for estimating biogeochemical processes, the current work can serve as the basis for future work to investigate spatiotemporal variations in biogeochemical rates and enhanced management strategies, to assess nutrient flushing rates from parent materials, to estimate native riparian buffer nutrient removal rates, and surface water – shallow groundwater nutrient loading within the central U.S.

4.5. Acknowledgements

Funding was provided by the Environmental Protection Agency (EPA) Region 7 (Grant Number: CD-97701401-0). Results presented may not reflect the views of the EPA and no official endorsement should be inferred. Gratitude is extended to multiple members of the Interdisciplinary Hydrology Lab (IHL) of the University of Missouri, School of Natural Resources. Sincere gratitude is extended to Stephen Pallardy and Kevin Hosman for climate data and valuable information about the BREA, and multiple reviewers whose comments greatly improved the quality of the manuscript.

4.6. References

Addy, K., A. Gold, P. Groffman, and P. Jacinthe (1999), Ground water nitrate removal in subsoil of forested and mowed riparian buffer zones, Journal of environmental quality, 28(3), 962-970.

Ambus, P., and R. Lowrance (1991), Comparison of denitrification in two riparian soils, Soil Science Society of America Journal, 55(4), 994-997.

Anderson, M. P., and W. W. Woessner (1992), Applied groundwater modeling: simulation of flow and advective transport.

Belden, A. C., and S. G. Pallardy (2009), Successional trends and apparent Acer saccharum regeneration failure in an oak-hickory forest in central Missouri, USA, Plant Ecol., 204, 305-322, doi: 10.1007/s11258-009-9593-4.

Bentrup, G. (2008), Conservation buffers: design guidelines for buffers, corridors, and greenways, US Department of Agriculture, Forest Service, Southern Research Station.

Burt, T. P., L. S. Matchett, K. W. T. Goulding, C. P. Webster, and N. E. Haycock (1999), Denitrification in riparian buffer zones: the role of floodplain hydrology, Hydrol. Process., 13, 1451-1463.

Burt, T., G. Pinay, and S. Sabater (2010), What do we still need to know about the ecohydrology of riparian zones?, Ecohydrology, 3(3), 373-377.

Burt, T., G. Pinay, F. Matheson, N. Haycock, A. Butturini, J. Clement, S. Danielescu, D. Dowrick, M. Hefting, and A. Hillbricht-Ilkowska (2002a), Water table fluctuations in the riparian zone: comparative results from a pan-European experiment, J. Hydro., 265, 129-148, doi: 10.1016/S0022-1694(02)00102-6.

Burt, T., P. Bates, M. Stewart, A. Claxton, M. Anderson, and D. Price (2002b), Water table fluctuations within the floodplain of the River Severn, England, J. Hydrol., 262, 1-20., doi: 10.1016/S0022-1694(01)00567-4.

Carsel, R. F., R. S. Parrish, R. L. Jones, J. L. Hanse, and R. L. Lamb (1988), Characterizing the uncertainty of pesticide leaching in agricultural soils, Journal of contaminant hydrology, 2, 111-124.

Cey, E. E., D. L. Rudolph, R. Aravena, and G. Parkin (1999), Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in southern Ontario, Journal of contaminant hydrology, 37(1), 45-67.

Clément, J. C., L. Aquilina, O. Bour, K. Plaine, T. P. Burt, and G. Pinay (2003), Hydrological flowpaths and nitrate removal rates within a riparian floodplain along a fourth-order stream in Brittany (France), Hydrological Processes, 17(6), 1177-1195.

Critchfield, H. J., (1966), General climatology. Prentice-Hall, Englewood Cliffs, New Jersey.

Dottori, F., M.L.V. Martina, and E. Todini (2009), A Dynamic Rating Curve Approach to Indirect Discharge Measurement. Hydrol. Earth Sys. Sci., 13, 847-863.

Enyart, D. (2009), Missouri Woody Biomass Harvesting: Best Management Practices Manual, Missouri Department of Conservation, Forestry Division, Jefferson City, MO, 42.Fetter, C. W. (1994), Applied hydrogeology, Prentice Hall Nueva Jersey.

Fleckenstein, J. H., S. Krause, D. M. Hannah, and F. Boano (2010), Groundwater-surface water interactions: new methods and models to improve understanding of processes and dynamics, Advances in Water Resources, 33(11), 1291-1295.
Freeze, R. A., and J.A. Cherry (1979), Groundwater. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.
Gooseff, M. N., S. M. Wondzell, R. Haggerty, and J. Anderson (2003), Comparing transient storage modeling and residence time distribution (RTD) analysis in geomorphically varied reaches in the Lookout Creek basin, Oregon, USA, Advances in Water Resources, 26(9), 925-937.
Gu, L., T. Meyers, S. G. Pallardy, P. J. Hanson, B. Yang, M. Heuer, K. P. Hosman, Q. Liu, J. S. Riggs, and D. Sluss (2007), Influences of biomass heat and biochemical energy storages on the land surface fluxes and radiative temperature, J. Geophys. Res., 112, 1-11, doi: 10.1029/2006JD007425.
Harbaugh, A. W. (2005), MODFLOW-2005: The US Geological Survey Modular Ground-water Model--the Ground-water Flow Process, US Geological Survey Reston, Virginia.
Harbaugh, A. W., and M. G. McDonald (1996), User's documentation for MODFLOW-96, an update to the US Geological Survey modular finite-difference ground-water flow model, US Department of the Interior, US Geological Survey.
Harbaugh, A. W., E. R. Banta, M. C. Hill, and M. G. McDonald (2000), MODFLOW-2000, the US Geological Survey modular ground-water model: User guide to modularization concepts and the ground-water flow process, US Department of the Interior, US Geological Survey.
Harrington, G. A., G. R. Walker, A. J. Love, and K. A. Narayan (1999), A compartmental mixing-cell approach for the quantitative assessment of groundwater dynamics in the Otway Basin, South Australia, Journal of Hydrology, 214(1), 49-63.
Haycock, N., and G. Pinay (1993), Groundwater nitrate dynamics in grass and poplar vegetated riparian buffer strips during the winter, Journal of environmental quality, 22(2), 273-278.
Hefting, M., B. Beltman, D. Karssenberg, K. Rebel, M. van Riessen, and M. Spijker (2006), Water quality dynamics and hydrology in nitrate loaded riparian zones in the Netherlands, Environmental Pollution, 139(1), 143-156.
Hensel, B. R., R. C. Berg, and R. A. Griffin (1990), Numerical Estimates of Potential for Groundwater Contamination from Land Burial of Municipal Wastes in Illinois. Illinois State Geological Survey EG 134. 84pp.
Hunt, R. J., D. T. Feinstein., 2012. MODFLOW-NWT: Robust Handling of Dry Cells Using a Newton Formulation of MODFLOW-2005, Ground Water, 50, 659-663, doi: 10.1111/j.1745-6584.2012.00976.x.
Hynes, H.B.N., (1983), Groundwater and stream ecology. Hydrobiologia. 100, 93-99.
Jacobs, T., and J. Gilliam (1985), Riparian losses of nitrate from agricultural drainage waters, Journal of environmental quality, 14(4), 472-478.
Jones, J.B., and P. J. Mulholland (2000), Streams and Groundwater. Elsevier Publishing Co., San Diego, CA., 120-190.

Jordan, T. E., D. L. Correll, and D. E. Weller (1993), Nutrient interception by a riparian forest receiving inputs from adjacent cropland, Journal of environmental quality, 22(3), 467-473.
Kasahara, T., and S. M. Wondzell (2003), Geomorphic controls on hyporheic exchange flow in mountain streams, Water Resources Research, 39(1), 1005.
Lautz, L. K., and D. I. Siegel (2006), Modeling surface and ground water mixing in the hyporheic zone using MODFLOW and MT3D, Advances in Water Resources, 29(11), 1618-1633.
Lee, S., K. Min, N. Woo, Y. Kim, and C. Ahn (2003), Statistical models for the assessment of nitrate contamination in urban groundwater using GIS, Environmental Geology, 44(2), 210-221.
Levia, D. F., D. E. Carlyle-Moses, and T. Tanaka (2011), Reflections on the State of Forest Hydrology and Biogeochemistry, 729-733 pp., Springer, London.
Lowrance, R., G. Vellidis, and R. K. Hubbard (1995), Denitrification in a restored riparian forest wetland, Journal of environmental quality, 24(5), 808-815. Hill, A. R. (1996), Nitrate removal in stream riparian zones, Journal of environmental quality, 25(4), 743-755.
Luo, Y., and M. Sophocleous (2010), Seasonal groundwater contribution to crop-water use assessed with lysimeter observations and model simulations, J. Hydrol., 389, 325-335., doi: 10.1016/j.jhydrol.2010.06.011.
McDonald, M. G., A. W. Harbaugh, and S. Book (1988), A modular three-dimensional finite-difference ground-Water flow model, in Techniques of Water-resources Investigations of the United States Geological A1, 586, edited.
McDonald, M. G., and A. W. Harbaugh (1984), A modular three-dimensional finite-difference ground-water flow model, Scientific Publications Company.
McDonald, M. G., and A. W. Harbaugh (2003), The history of MODFLOW, Ground Water, 41(2), 280-283.
Moriasi, D. N., J. G. Arnold, M. W. Liew, R. L. Bingner, R. D. Harmel, and T. L. Veith (2007), Model evaluation guidelines for systematic quantification of accuracy in watershed simulations, Transactions of the ASABE, 50, 885-900.
MSDIS, 2009: Missouri Spatial Data Information Service (Online). Available from: http://msdis.missouri.edu/ (Accessed August 2012).
Nash, J. E., and J. Sutcliffe (1970), River flow forecasting through conceptual models part I—A discussion of principles, J. Hydrol., 10, 282-290, doi: 10.1016/0022-1694(70)90255-6.
Pallardy, S., T. Nigh, and H. Garrett (1988), Changes in forest composition in central Missouri: 1968-1982, Am. Midl. Nat., 120, 380-390.
Peterjohn, W. T., and D. L. Correll (1984), Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest, Ecology, 65(5), 1466-1475.
Pollock, D. W. (1994), User's Guide for MODPATH/MODPATH-PLOT, Version 3: A Particle Tracking Post-processing Package for MODFLOW, the US: Geological Survey Finite-difference Ground-water Flow Model, US Department of Interior.

Reed, S.E., (2010), Ambrosia Beetle Habitat Use, Host Use, and Influence on Early Wood Colonizing Microbes in an Oak-Hickory Forest In Forestry. University of Missouri: Columbia, Missouri.

Rochow, J. J., (1972), A vegetational description of a mid-Missouri forest using gradient analysis techniques, Am. Midl. Nat., 377-396.

Schilling, K., and Y. K. Zhang (2004), Baseflow contribution to nitrate-nitrogen export from a large, agricultural watershed, USA, Journal of Hydrology, 295(1), 305-316.

Sophocleous, M. (2002), Interactions between groundwater and surface water: the state of the science, Hydrogeo. J., 10, 52-67, doi: 10.1007/s10040-001-0170-8.

Storey, R. G., K. W. F. Howard, and D. D. Williams (2003), Factors controlling riffle-scale hyporheic exchange flows and their seasonal changes in a gaining stream: A three-dimensional groundwater flow model, Water Resour. Res., 39(2), 1034.

Strahler, A., (1952), Hypsometric (area-altitude) analysis of erosional topography, Bull.Geol. Soc. Am, 63, 1117-1142.

Swanson, F. J., and S. M. Wondzell (1996), Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream. II: Nitrogen cycling, Journal of the North American Benthological Society, 20-34.

US Department of Agriculture, N. R. C. S. (2009), Web Soil Survey.

Willmott, C. J., (1981), On the validation of models. Phys. Geogr., 2, 184-194.

Woessner, W. W. (2000), Stream and fluvial plain ground water interactions: rescaling hydrogeologic thought, Ground Water, 38(3), 423-429.

Wondzell, S. M., and F. J. Swanson (1996), Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream. II: Nitrogen cycling, Journal of the North American Benthological Society, 20-34.

Wroblicky, G. J., M. E. Campana, H. M. Valett, and C. N. Dahm (1998), Seasonal variation in surface-subsurface water exchange and lateral hyporheic area of two stream-aquifer systems, Water Resources Research, 34(3), 317-328.

Young, F. J., C. A. Radatz, and C. A. Marshall (2003), Soil Survey of Boone County, Missouri Natural Resources Conservation Service, 25 – 35.

Zheng, C., and G. D. Bennett (1995), Applied contaminant transport modeling: Theory and practice, Van Nostrand Reinhold New York.

Zheng, C., and P. P. Wang (1999), MT3DMS: a modular three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems; documentation and user's guide, Rep., DTIC Document.

CHAPTER V: CONCLUSIONS AND SYNTHESIS

5.1. Summary

In this dissertation, a practical approach to quantify and predict surface water (SW) – shallow groundwater (GW) connectivity was presented. This research represents the first (to the author's knowledge) study to present SW-GW hydrologic and nutrient interaction results, from both field monitoring and numerical modeling methods for an Ozark border forest in the karst hydrogeological system and humid-continental climatic region of central U.S. The research provides improved understanding of SW-GW hydrological connectivity in the region, as well as assessment of management tools that will lead to reduced riparian zone management costs through better validation and application of management practices.

Advances in riparian zone management require innovative reach-scale experimental studies that will result in increased process based understanding leading to improved management tools (e.g. models), that are calibrated and validated against physical observations (Levia *et al*., 2011; Burt *et al*., 2010; Jones and Mulholland, 2000). Aside from lacking quantifiable validation, riparian zone best management practices seldom take into account water and nutrient dynamics between SW and GW, particularly in the Ozark forested regions of Mid-Missouri in the central U.S., where the presence of karst geology, Ozark hardwood vegetation and humid-continental climate can result in complex hydrologic and nutrient interactions between SW and riparian zone GW.

The overall objective of this dissertation research was to improve the understanding of spatiotemporal variations in SW-GW hydrologic and nutrient interactions in the karst hydrogeological, humid-continental climatic region of an Ozark border forest of Missouri, central U.S. Specific objectives were to (a) Quantify spatiotemporal variations in hydrologic flux between a mid - Missouri stream and forested riparian zone; (b) Quantify spatiotemporal variations in nutrient concentration (i.e. Nitrate, Potassium, Phosphorus and Ammonium) dynamics between a mid – Missouri stream and forested riparian zone; and (c) Use MODFLOW and HYDRUS 1D to predict hydrologic and nutrient flux in a forested riparian terrain of central Missouri, and compare modeling outputs to observations with the help of statistical analyses.

5.1.1. Stream water – shallow groundwater hydrologic interactions

This investigation focused on SW-GW hydrologic interactions . High-resolution (i.e. five minute) data showed average groundwater flux of -3 x 10^{-5} m^3 s^{-1} m^{-1} (losing stream) for the entire study reach (total reach length = 830m) during the WY 2011 . Results indicate rapid groundwater response to rainfall events within 2 to 24 hours as much as nine meters from the stream. Data analyses indicated stream flow loss of 28 and 7% to groundwater during winter and spring, respectively. During the dry season, the stream was gaining 95% of the time. During the wet season, the stream was losing 70% of the time. Based on established assessment criteria, shallow groundwater modeling performance with HYDRUS – 1D was deemed '*Very good*' (NS = 0.95, r^2 = 0.99, RMSE = 2.38 cm and MD =1.3 cm). Modeling results indicated a high hydraulic conductivity value of 1.5×10^{-5} m s^{-1} at the study sites, indicating rapid groundwater movement in the subsurface. This work also identified multiple considerations that if addressed will lead to improvements of the HYDRUS 1-D groundwater modeling, including negligible difference in results (<2%) between runs with finer and coarser mesh size. Finally, this study demonstrated the need to construct robust three dimensional groundwater models to simulate SW-GW interactions and spatiotemporal variations in SW-GW hydrologic connectivity in order to appropriately develop accurate means to effectively estimate groundwater storage in the Ozark forested riparian zones of central U.S.

5.1.2. Stream water – shallow groundwater nutrient interactions

Information pertaining to spatiotemporal variation in SW-GW nutrient concentrations, relative to variations in the hydrologic regime, is limited in the central U.S. and in varying geologic settings (Sophocleous, 2002). Nitrate (NO_3^-), total phosphorous (P), potassium (K) and ammonium (NH_4^+) concentrations were quantified between SW and neighboring riparian zone GW over the 2011 water year in an Ozark border mixed-hardwood forest of mid-Missouri, central U.S. Observed seasonal NO_3^- concentration patterns of winter maxima and summer minima in SW and GW were similar to previous U.S. studies in hardwood forests, without karst geology, indicating that the rate of nutrient cycling by biochemical processes in hardwood forests were comparable to the nutrient cycling by geochemical processes in a deciduous forest. Annual average stream water NO_3^- concentration decreased at downstream locations, by 21, 38 and 38% at SII, SIII and SIV, respectively, relative to stream water nitrate measured at SI (0.53 mg L^{-1}). Similarly, annual average stream water total phosphorus concentration decreased at downstream locations, by 15, 31 and 46% at SII, SIII and SIV respectively, relative to that at SI (0.13 mg L^{-1}). Annual average K for stream water increased at SII and SIII by 15 and 1% relative to that measured at SI (3.29 mg L^{-1}). Annual average stream water NH_4^+ for downstream locations varied minimally relative to SI. Annual average NH_4^+ concentrations were 0.06, 0.07, 0.06 and 0.05 mg L^{-1}, at SI, SII, SIII and SIV respectively. Results of a hyperbolic model, used to quantify hydrological controls on stream water nutrient concentrations, indicated that NO_3^- and K exhibited dilution behavior while NH_4^+ had a concentration effect and P was hydrologically constant. Lower concentrations of nutrients in GW, relative to SW, indicate that the GW in karst geology, with low residence time and rapid water movement, is an efficient buffer in removing and retaining excess nutrients from water draining into the stream.

5.1.3. Modeling stream water – shallow groundwater interactions

The three-dimensional groundwater flow model, MODFLOW, paired with the nutrient transport model, MT3DMS, was used to investigate the hydrologic and nutrient dynamics between a second order stream and shallow aquifer in the riparian zone of a second growth Ozark border forest with karst hydrogeology, in the central U.S. In addition, a particle tracking module, MODPATH, was used to delineate hydrologically active SW-GW interaction zone and estimate spatiotemporal variations in flow length and residence time.

MODFLOW results indicated that Brushy Creek alternated between a gaining and losing stream throughout the study period, illustrating the complex hydrologic regime in this karst geological system. MT3DMS indicated that the unconfined aquifer received nitrate at the rate of 85.5 Kg N ha^{-1} yr^{-1} from the stream. Relative to results of studies in Beaverdam watershed in North Carolina (19.4 Kg N ha^{-1} yr^{-1}), a deciduous forest in Maryland (60.0 Kg N ha^{-1} yr^{-1}) and a stream valley fen in Denmark (390 Kg N ha^{-1} yr^{-1}), results are reasonable (except when compared against the results from Denmark in which the study site was adjacent to a cropland (the reader is referred to the review by Hill, 1996)). The annual average nitrate loading rate (85.5 Kg N ha^{-1} yr^{-1}) observed in this study is reasonable when compared to the annual average rate of 75.4 Kg N ha^{-1} yr^{-1} observed at 14 temperate deciduous forests by Whittaker and Likens (1975), and hence the nitrate loading in the riparian zone at BREA is under the range that can be processed by biochemical nutrient cycling (i.e. vegetation uptake). MODPATH results indicated that the lateral extent of SW-GW interactions at the two sites (PZI and PZII) had significant spatial variations ($p = 0.089$) but temporal variations were not significant ($p = 0.45$). Modeling results demonstrated that MODFLOW can be implemented with confidence to predict groundwater head distribution (NS = 0.47, $r^2 = 0.77$, RMSE = 0.61 cm and MD =0.46 cm). MT3DMS indicated that the highest NO_3^- loading of 707 Kg d^{-1} from the stream to the aquifer occurred in the winter season. MT3DMS results also indicated that the effective stream nitrate loading lateral extent in the riparian zone varied seasonally ($p = 1.5 \times 10^{-8}$). Annual average lateral distance of nitrate loading from the stream was 70 m, indicating that the current statewide streamside best management plans (BMPs) for buffer width, of 15 m, will not be sufficient to cover the entire extent of nitrate loading and prevent excess nutrient loading in the stream. Hence, current BMPs need to be reconsidered to prevent excess nutrient loading in the shallow aquifer. MODPATH revealed significant spatiotemporal variations, between sites PZI-PZII, ($p < 0.05$) in subsurface flowpath and travel time, ranging from 213 m and 3.6 years to 197 m and 11.6 years. The variations in lateral extent of SW-GW interaction length (10 to 50 m) indicate that the current state recommendations for buffer width (15 m) need to be validated with respect to field and model observations of SW-GW interactions.

5.2. Synthesis

The preceding work enabled estimations of spatiotemporal variability in SW-GW hydrologic and nutrient interactions for the BREA watershed using physical observations and numerical models to predict SW-GW interactions. The results of this study are of particular importance for land managers wishing to formulate riparian zone management plans for post-harvest conditions, or other development situations. For example, shallow groundwater flow towards or away from a given stream could be partially regulated by deep rooted native vegetation. That same vegetation could also serve to increase infiltration, percolation and recharge thus maintaining pre-harvest/development connectivity between riparian zone vegetation and the shallow groundwater aquifer.

MODFLOW results can aid in identifying such locations for implementing variable buffer widths by analyzing variations in net shallow groundwater flow direction. Using numerical models (e.g. MODFLOW and HYDRUS-1D), land managers could identify losing streams, by analyzing loss in stream flow at downstream locations (with subsequent rise in groundwater head in adjoining riparian zone indicating lateral movement of water), and apply suitable management plans to prevent groundwater pollution from excess stream water input. This study showed nitrate loading from the SW to the GW, therefore, to reduce GW nitrate concentrations in the riparian zone, management plans should include methods that increase organic matter content in soil that promote denitrification (Bentrup, 2008). For example vegetation with adequate rooting depth, dense root biomass and vegetation that is tolerant to seasonal water table fluctuations are more suitable for preventing shallow groundwater contamination in regions where SW input to GW is high (Bentrup, 2008). Current Best Management Plans (BMPs) for timber harvest, for the state of Missouri, include recommendations for a 7.6 m wide primary buffer strip, followed by a secondary buffer strip of varying width depending on the slope (Enyart, 2009). However, there is no mention of stream orders to which these recommendations apply and there is no mention about buffer species selection and riparian stand density. According to Enyart (2009), a 15 m buffer width is recommended for the study sites at Baskett. Based on this study, a variable buffer width will be more suitable to prevent excess nutrient loading in Brushy Creek at locations where the stream is gaining. As per Bentrup (2008), a wider and larger (greater than 15 m) forested buffer strip is required at locations where GW contributes to greater nutrient loads. The need for wider buffer strips is consistent with the findings of Bulliner (2011) who indicated that at least 25 to 40 m is necessary to protect stream channels from stream heating processes that may otherwise be increased in post-harvest conditions. Based on the current study's results, the SW-GW active area extends to at least 70 m from the stream bank. Modeling results from the current work that showed that the stream shallow groundwater mixing occurred as far as 70 m from the streambank. Therefore, a buffer width of 70 m is recommended for the study sites at BREA to regulate SW-GW hydrologic and nutrient interactions. The buffer vegetation type should include native plants with roots that intercept subsurface flow, native plants with higher root biomass, native plants tolerant of wet soils and high nutrient levels and non-nitrogen fixing plants and have an appropriate stand density that can reduce surface runoff and promote infiltration, percolation and rapid movement of water through preferential flow paths (Bentrup, 2008).

Stream water phosphorus was shown to be hydrologically constant. Therefore, caution should be observed when implementing management plans that may include application of fertilizers with phosphorus as any excess phosphorus might not be observed in the soil for plant uptake, but will be washed to the stream, thus polluting surface water.

The successful prediction of complex hydraulic head distributions by MODFLOW and HYDRUS-1D in a karst hydrogeology will increase awareness in the use of numerical models (especially MODFLOW and HYDRUS-1D) in quantifying SW-GW interactions and aid in testing aforementioned management scenarios before implementation.

5.3. Future research

During the course of this investigation, other SW and GW physical parameters, including pH, electrical conductivity (EC), total dissolved solutes (TDS) and salinity were also collected. Water pH, EC, TDS and salinity data can be used as important indicators for water quality (Patni *et al*., 1998; Hill and Neal, 1997), however very few studies have compared water physical parameters against water nutrient concentration levels, in particular, studies are limited in karst hydrogeological systems (Ford and Williams, 2007). Since the current study results, using stream and groundwater head data, indicate that SW and GW nutrient concentrations are greatly influenced by SW-GW hydrologic interactions, future research is warranted to focus on comparing water physical parameters against water nutrient concentration levels. Such research will lead to, as indicated by Hill and Neal (1997), Patni *et al*. (1998) and listed in a review by Levia *et al*. (2011), innovative use of easily obtained and cost effectively available water physical parameter data (relative to hydraulic head values from wells) to quantify SW-GW interactions. In addition, analysis of spatiotemporal variations in water physical parameters, relative to spatiotemporal variations in water nutrient concentrations, could be vital to understand effects of seasonal variations and effects due to downstream versus upstream locations. Shallow groundwater pH levels could reflect the soil's acidity and could exhibit temporal variability due to seasonal changes in soil water content (Patni *et al*., 1998). Hill and Neal (1997) measured pH and EC at the River Severn Catchment in Mid Wales, UK, to examine the extent of spatial and temporal variation in stream and groundwater chemistry. They found that groundwater pH and EC data were as effective as groundwater nutrient concentration data to identify spatial and seasonal variations in groundwater quality. They concluded that catchment scale hydrological models should include simple water quality indicators (especially pH and EC) as chemical finger printing parameters to effectively identify areas of contrasting weathering. Considering their success in using pH and EC data to monitor groundwater quality, the SW and GW-pH and EC time series data collected over the 2011 water year at Baskett could also be used to better understand groundwater quality with seasonal and spatial variations.

In general, future work should focus on cost effective methods to collect water quality parameters to estimate land-use impacts on SW-GW hydrobiogeochemical interactions. Results of such work are vital for understanding complex hydrologic processes from a water physical parameter perspective, in particular, in karst hydrogeological systems in regions where field in-situ water quality measurements are often more feasible than lab analysis (for example when transportation of water samples can induce error in the results) (Levia *et al*., 2011; Jones and Mulholland, 2000; Burt *et al*., 2010).

5.4. Closing Comments

Scientists stress the need to develop interdisciplinary approaches to understand biogeochemical processes that affect nutrients at the SW–GW interface and to quantify influence of nutrient dynamics on aquatic (stream) and terrestrial (especially in the riparian zone) ecosystems. The development of such interdisciplinary approaches will aid in the formulation of physical process based management plans that can reduce excess nutrient loading in SW and GW. This development is of particular importance in headwater systems since they serve as key sites for nutrient retention, and in karst hydrogeological environments. In the past, less attention to hydrology (especially shallow groundwater) has led to uncertainties in estimates of nutrient flux occurring in the riparian zone. The overall results from this study emphasize the significance of local climate and spatial variations in regulating the magnitude of the shallow groundwater regime and the variability of nutrient SW-GW exchange with variations in the GW regime. Study sites with an integrated, interdisciplinary and physical-process based numerical approaches, like that in BREA, aid in the identification of key nutrient cycling pathways and improve process based understanding. The numerical models, used in this study, can be applied (after proper calibration and validation) to other riparian zones (especially with karst geology), where large stream water – shallow groundwater hydrologic and nutrient fluxes occur to identify key biogeochemical nutrient pathways. Progress in identification of key biogeochemical pathways will prove extremely beneficial for management, protection and restoration of surface water and riparian zone ecosystems.

5.5. References

Bentrup, G., 2008. Conservation buffers: design guidelines for buffers, corridors, and greenways, US Department of Agriculture, Forest Service, Southern Research Station. General technical report SRS-109.

Bulliner, E., 2011. Quantifying riparian canopy energy attenuation and stream temperature using an energy balance approach, In *Forestry*. University of Missouri: Columbia, Missouri.

Burt, T., G. Pinay, and S. Sabater (2010), What do we still need to know about the ecohydrology of riparian zones?, Ecohydrology, 3(3), 373-377.

Enyart, D., 2009. Missouri Woody Biomass Harvesting: Best Management Practices Manual, Missouri Department of Conservation, Forestry Division, Jefferson City, MO, 42.

Ford, D. C., and P. Williams (2007), Karst hydrogeology and geomorphology, Second ed., John Wiley and Sons, New Jersey, USA.

Hill, A. R., 1996. Nitrate removal in stream riparian zones, J. Environ. Qual., 25, 743-755.

Hill, T., and C. Neal (1997), Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater for the Upper River Severn catchment, Hydrology and Earth System Sciences Discussions, 1(3), 697-715.

Jones, J.B., and P. J. Mulholland (2000), Streams and Groundwater. Elsevier Publishing Co., San Diego, CA., 120-190.

Levia, D. F., D. E. Carlyle-Moses, and T. Tanaka (2011), Reflections on the State of Forest Hydrology and Biogeochemistry, 729-733 pp., Springer, London.

Patni, N., L. Masse, and P. Jui (1998), Groundwater quality under conventional and no tillage: I. Nitrate, electrical conductivity, and pH, Journal of environmental quality, 27(4), 869-877.

Sophocleous, M. (2002), Interactions between groundwater and surface water: the state of the science, Hydrogeo. J., 10, 52-67, doi: 10.1007/s10040-001-0170-8.

Whittaker, R., and G. Likens (1975), Primary Productivity of the Bio2 sphere, edited, Springer.

VITA

Pennan Chinnasamy was born in Zurich, Switzerland in 1980. Until the age of seven, he was raised in the U.S, and then returned to India. He did most of his schooling in Chennai of Tamil Nadu, India. He obtained his bachelor's degree in Physics from Swami Vivekananda College, affiliated to the University of Madras, located in Chennai of Tamil Nadu, India. He obtained his master's degree in Physics from Sri Mad Andavan College, affiliated to the Bharathidasan University, located in Srirangam, Thiruchirappalli of Tamil Nadu, India. In January of 2007, he moved to the U.S. and in 2009, obtained his master's degree in Physics from Wesleyan University, Connecticut. During the fall of 2009, he switched disciplines from Physics to Hydrology and matriculated at the University of Missouri, Columbia, to pursue his doctoral degree. He received his graduate certification in Geographic Information Systems (GIS) in 2011.