Seasonal Variations in Nitrate Flux, Transport, and Sources in the Upper Illinois River Basin

BY

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DISSERTATION

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DEDICATION

To my dad. Thanks for your faith in me.

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CONTRIBUTION OF AUTHORS

Chapter I is a review on study objectives, study area, and methods, where I discuss why and how I conducted my studies. Chapter II represents a manuscript that will be published in the future, for which I was the primary author of the research. Dr. J.K. Böhlke and my advisor, Dr. Neil Sturchio advised me through the entire research, and contributed to the manuscript revisions. Sheng Huang and Dr. Miquel Gonzalez-Meler contributed to the design of the project and data analysis at an early stage. Chapter III represents a manuscript that will be submitted for publication for which I was the primary author and driver of the work. Dr. Eugene Yan and Dr. Yonas Demissie contributed greatly to the model construction and associated work. Dr. J.K. Böhlke and Dr. Neil Sturchio instructed me and provided constructive advice on the work. Chapter IV is my summary of the research presented in this dissertation.

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LIST OF ABBREVIATIONS

AC	Aux Sable Creek
BC	Bureau Creek
CBMP	Illinois Council on Best Management Practices
CDL	cropland data layer
CIAAW	Commission on Isotopic Abundances and Atomic Weights
CENR	National Science and Technology Council, Committee on Environment and Natural Resources
DEM	digital elevation maps
DO	dissolved oxygen
DP	Des Plaines River
DR	DuPage River
EIGL	Environmental Isotope Geochemistry Laboratory
EPA	Environmental Protection Agency
Fe	iron
FR	Fox River
HRU	hydrologic response units
IAEA	International Atomic Energy Agency
KR	Kankakee River
MR	Mazon River
MRB	Mississippi River Basin
MWRDGC	Metropolitan Water Reclamation District of Greater Chicago
N	nitrogen
N_2	nitrogen gas
NAWQA	National Water-Quality Assessment
NH_4	ammonium
NGRM	northern Gulf of Mexico
NO_3	nitrate
O	oxygen
RSIL	Reston Stable Isotope Laboratory

SL	Senachwine Lake
SWAT	Soil and Water Assessment Tool
SWRP	Stickney Wastewater Reclamation Plant
UIRB	Upper Illinois River Basin
USDA	U.S. Department of Agriculture
USEPA	Environmental Protection Agency
USGS	US Geological Survey
VSMOW	Vienna Standard Mean Ocean Water
VR	Vermillion River
WHO	World Health Organization
WRP	wastewater reclamation plant
WTP	wastewater treatment plant

SUMMARY

By introducing excess N into the environment via the production of food and energy, humans have remarkably changed the biogeochemical cycles of nitrogen and the ecosystem. Excess N contributes to numerous environmental issues such as eutrophication, hypoxia, and loss of habitat and biodiversity. The EPA Gulf Hypoxia Action Plan provides nutrient reduction strategies targeting at least a 45% reduction in riverine total nitrogen load.

This study was conducted to study the sources, inventory, and transport of nitrate in the Upper Illinois River Basin (UIRB)—one of the basins with the highest N delivery amount and rate to the Gulf of Mexico. We combined the two most powerful approaches for the study of N: isotopic/chemical measurements and hydrological modeling were integrated on basin and subbasin levels to gain full understanding of N behavior in the UIRB, in order to assist people to make scientific and efficient management plans for N control and reduction.

River samples were collected on the Upper Illinois River and its major tributaries from 2004 to 2008, in order to gain useful information on the basin nutrient transport and mixing processes. The measurements of nitrate concentration and isotopic values of water samples provided us with insights into the major sources of nitrate and its seasonal and temporal variations, which were indicators for studying land use impact on nutrient transport, and in-stream processes within the basin. Our study demonstrated that isotopic composition of nitrate is controlled by land use patterns, weather, and location. The

influence of wastewater effluents, tributary inputs, and agricultural land on nitrate concentration and isotopic values were well documented.

Potential increase in N fertilizer use is expected for expanding production of corn and cellulosic materials. SWAT (Soil and Water Assessment Tool) simulations of various fertilizer application scenarios were conducted to study the direct impact of changes in fertilization on N export and crop output respectively at basin and subbasin levels. SWAT also yielded outputs that assist us to understand in-stream denitrification processes, basin nitrate export mechanisms, and control of hydrological conditions on denitrification and N transport at basin and subbasin levels. The SWAT model results are consistent with results of the geochemical study of UIRB nitrate. SWAT simulations also add missing pieces to the understanding of environmental N behavior within the UIRB.

This study demonstrates that there are huge potential benefits in modeling and geochemical studies that will allow us to enhance our knowledge of management of N and N sources and sinks, which are required to achieve the extremely challenging nitrogen reduction goal.

CHAPTER 1

1. INTRODUCTION

Humans have remarkably altered biogeochemical cycles of nitrogen and thus the ecosystem by introducing excess nitrogen (N) to the environment. Anthropogenic nitrogen enters the environment through synthetic N fertilizer production and use, deposition from fossil fuel combustion, livestock manure, urban sewage discharge, and N fixation by cultivated leguminous crops (Galloway, 2004). Excess N contributes to numerous negative impacts on human health and environment, including loss of habitat and biodiversity, eutrophication, hypoxia, increase in blooms of harmful algae, and fish kills (Seitzinger et al., 2010; Rabalais, 2001). Both the social/environmental damage caused by excess N and the cost to mitigate N input to the environment are significant (Dodds, 2008; Sobota, 2014). It is estimated that the strategies for reducing agriculture-related nutrients alone cost a total of $600 million for each U.S. state (Secchi et al., 2007).

This study was thus conducted to study the sources and inventory of environmental N and its transport and mixing mechanisms in the Upper Illinois River. Despite numerous studies that have been done to study environmental N worldwide, there has not been much work published that combines the two powerful approaches for N study: isotopic/chemical measurements and numerical hydrologic modeling. Isotopic/chemical measurements are integrated with hydrologic modeling on basin scale in this study to gain further understanding of N behavior in the environment, and to provide background information in order to help achieve the nitrate (NO_3^-) reduction goal in Illinois.

There are four chapters in this dissertation, including an introduction to the study objectives and methods (Chapter 1); two papers to be published—a paper studying seasonal variations in nitrate flux and isotopic compositions in the Upper Illinois River Basin (Chapter 2), a numerical rainfall-runoff model based on the Soil and Water Assessment Tool (SWAT) software that simulates nitrate sources, transport, and denitrification within the Upper Illinois River watershed (Chapter 3); and a final chapter that summarizes the results and conclusions of this study (Chapter 4).

1.1. Introduction to nitrogen (N)

Nitrogen (N) has an atomic number of 7 and standard atomic weight of 14.0067 (CIAAW, 2013). N has its electron configuration as $2s^2 2p^3$. Nitrogen is reactive due to its ability to exist in multiple valence states. It is the lightest pnictogen and one of the most common elements in the universe. On the earth, the element N makes up about 78% of the atmosphere in the form of nitrogen gas, N_2 (Figure 1), which accounts for 2% of the total N abundance on the Earth. The strong triple bond in N_2 dominates nitrogen chemistry, causing it to be inactive at standard temperature and pressure, and thus difficult to be converted to other compounds by organisms or industrial processes.

There are two stable isotopes of N: ^{14}N and ^{15}N, the atomic masses of which are 14.0031 and 15.0001, respectively (CIAAW, 2013). With a natural abundance of 99.632%, ^{14}N makes up the majority of naturally occurring nitrogen. ^{15}N has an abundance of 0.367%. Because the low abundance of ^{15}N in air is constant, the isotopic composition of N_2 in air is used as the standard reference for reporting $\delta^{15}N$ values (USGS, web resource). There are also fourteen radioactive isotopes of N, with atomic masses ranging from 10 to 25, with half-lives ranging from less than 10 minutes to less than a second.

Nitrogen has several forms in different valence states, from the most oxidized form—nitrate (Figure 1), where nitrogen has a +5 valence state, to the most reduced form – ammonia gas or ammonium, where nitrogen has a -3 valence state. The N cycle is one of the most important chemical/biochemical cycles in our environment. It is fundamental in supporting life on Earth, and in driving the biological cycle. Figure 2 illustrates the major compounds in the biogeochemical N cycle and the reactions involved.

Because of its important biological functions, the greatest commercial use of N is for the manufacture of fertilizers, including forms of ammonia, ammonium, nitrogen solutions, sodium nitrate, and urea. According to the U.S. Department of Agriculture (USDA) statistics, the domestic consumption of ammonia fertilizer in 2008 was over 4.4 million tons, about 3 times larger than that of the 1960s'. The consumption of ammonium fertilizer in 2008 was over 2.2 million tons, compared to 1.8 million tons in 1963. The usage of nitrogen solutions increased from 0.7 million tons in 1963, to 11.4 million tons in 2008; the usage of urea also increased by 39 times in the past forty years (USDA, 2008).

1.2. Nitrate pollution

Nitrogen (N) plays an essential role in plant growth and many activities of living organisms as it is a key component of nucleic acids, amino acids, proteins, and coenzymes (Hodge, 2005; Li et al., 2013; Mengel and Kirkby, 2001). Lack of N and other nutrients could hinder plant growth and cause many economic and ecological issues; however, excess N in the environment is also the root of many environmental problems. Over-enrichment of nitrogen induced by extensive human activities has caused many serious environmental issues such as water degradation and eutrophication (Justić et al., 2003; Rabalais, 2001; Turner and Rabalais, 1994). Eutrophication is the process by which an excess supply of nutrients leads to enhancement of primary production in the fresh water and marine ecosystems, noxious phytoplankton blooms, and bottom water hypoxia at coastal areas and lakes (Justić et al., 2003; Rabalais, 2001; Turner and Rabalais, 1994; Vitousek et al. 1997; Harrison et al. 2008). Hypoxia occurs when dissolved oxygen (DO) concentration is too low to sustain aquatic life, generally when

DO concentrations are below 2 mg/L. Oxygen is consumed by bacteria and other organisms during the decomposition of "excess" phytoplankton algae, the production of which is stimulated by increased nutrient load. In the United States (Alexander et al., 2008; CENR, 2000), the area affected by mid-summer bottom water hypoxia in the northern Gulf of Mexico has been larger than 10,000 km^2 since 1993, and was larger than 20,000 km^2 in 1999. Gulf ecosystems and fisheries are impacted by hypoxia (CENR, 2000), which has been attributed to the rise in riverine N flux (Alexander et al., 2008).

Direct toxicity of some algae is another problem in aquatic ecosystems resulting from excess nitrate (IAEA, 2013). According to the World Health Organization (WHO) report, direct or indirect nitrate intake via drinking water and food can cause acute or chronic poisoning of many species, including humans. While nitrate is a normal component of the human diet, its toxicity is primarily due to its conversion to nitrite by bacteria in the gastrointestinal system, in turn oxidizing normal hemoglobin to methemoglobin (Fe^{2+} to Fe^{3+}) which is unable to transport oxygen from lungs to the tissues, and this results in methaemoglobinaemia (WHO, 2011). Concentrations of methemoglobin above 10% may cause a bluish color of skin and lips (cyanosis), and values above 25% can lead to weakness, rapid pulse and tachypnea. Death may occur if methemoglobin values exceed 50-60% (USEPA, 2007).

In Europe, the nitrate levels in ground and surface waters often exceed the drinking water limit of 50 mg NO_3^- /L (Kendall & McDonnell, 1998). The US EPA's limit of nitrate in drinking water is 10 mg N/L (equivalent to 45 mg NO_3^- L^{-1}). However, WHO reports nitrate levels exceeding 20 mg N/L in about 3 % of surface waters and 6% of groundwater supplies (WHO, 2011).

1.3. Source of nitrate pollution

Nitrate is the most common inorganic form of N in soil and water. The sources of nitrate in the environment include the following: agricultural input (nonpoint sources) of nitrogen fertilizer and animal manure via tile drainage or leaching from soil, domestic or industrial nitrogen-bearing wastewater via sewage (point source), fossil fuel combustion and direct atmospheric deposition, and mineralization of soil organic nitrogen and biological nitrogen fixation (Nestler et al., 2011) Nonpoint sources contribute about 90% of the nitrogen in the Mississippi River Basin, with fertilizer and mineralized soil organic N as the dominant input (>50%) of the total N flux to the Gulf of Mexico (Chang et al., 2002). The usage of N fertilizer and the growth of N-fixing crops have altered the global N cycle (Vitousek, 1997). Studies showed that high nitrate concentrations are associated with particular land use patterns, typically basins with high percentage of land growing row crops such as corn or soybean, or a high population density, or both (Goolsby et al., 1999).

The Mississippi River is the largest river basin in North America, and it discharges to the Gulf of Mexico. About 58% of the Mississippi Basin is farmland, with extensive use of fertilizer and manure input. Since 1980, mean annual flux of total N from this basin to the Gulf of Mexico has been about 1.6 million metric tons (Goolsby et al., 1999)—it is now about three times larger than it was in the 1950s; nitrate concentrations have also increased two to five times in the last century (Goolsby et al., 1999). The Illinois River is a major tributary of the Mississippi River and flows through one of the most productive farming regions in the United States. According to a report from the Illinois Council on Best Management Practices in 2011, Illinois ranks the second in both corn and soybean production in the U.S. and third in agricultural exports. With this intensive food production, substantial increase in N input was observed, originating from fertilizer, plant fixation, and livestock manure, along with other sources. By the end of last century, the fertilizer consumption in Illinois was more than 400,000 tons N per year; the legume fixation of nitrogen as N was around 190,000 metric tons per year; and the manure input was around 50,000 tons per year. The mineralized soil N is also an important contribution to riverine nitrogen, which was about 400,000 tons per year in the same time frame. Municipal point sources contributed a smaller portion compared to other sources, but still reached 24,000 tons N per year in the 20th century. As a consequence, the concentration of riverine nitrate in the Illinois River has increased by more than two fold in the last century: the nitrate concentration in the Upper Illinois River was 1.89 mg/L in 1896-1899, and was 4.24 mg/L in 1980-1996; for the Lower Illinois River, nitrate concentration increased from 1.01 mg/L in 19th century to 4.12 mg/L by the end of last century (Goolsby et al., 1999).

It is urgent to improve nutrient management strategies within the Illinois River Basin in order to control annual nitrate flux to the Gulf of Mexico and to preserve water quality. However, identifying nitrate sources and understanding nitrogen transport mechanisms inside a basin can be challenging, due to complex mixing and transformation processes, such as nitrification, immobilization and denitrification, which are further complicated by the movement of water and sediments. The purpose of this study is to couple hydrologic modeling with geochemical studies of basin nitrate to acquire a better understanding of nitrate behavior and reactions, its various pathways within the watershed, and the seasonal/temporal variation in different sources and their apportionment. The results add insights into nutrient management plans to ameliorate eutrophication and hypoxia in the coastal areas.

1.4. Study objectives

A hydrologic model at the basin scale was constructed for the Upper Illinois River Basin (UIRB) using the Soil and Water Assessment Tool (SWAT). The model was applied to provide an integrated assessment of the effect of weather and land use management on basin nitrate export. Geochemical measurements of river samples were applied to decipher nitrate fate and transport, and their seasonal and spatial variation within the UIRB: a dual-isotope approach combined with nitrate concentration measurements was used to identify nitrate sources, mixing relationships, and the extent of biodegradation. The goals of this study are to acquire more comprehensive understanding of nitrate transport mechanisms along reaches, denitrification processes in soil water, shallow groundwater, and surface reaches, and how denitrification will affect nitrogen export, since in-stream denitrification rates are important to identify nitrate sources and to predict effects of land-use changes on downstream ecosystems (Böhlke et al., 2009). In order to provide advice on how to effectively achieve N reduction goals in the Upper Illinois River Basin towards the end of the 21st century, the calibrated SWAT model was also applied to predict basin nitrate output under different agricultural management scenarios.

1.5. Study area

1.5.1. Drainage area

The boundaries of the Upper Illinois River Basin in this study differ somewhat from those of the Upper Illinois River Basin studied in the National Water-Quality Assessment (NAWQA) program by the U.S. Geological Survey (USGS). The drainage area of the

NAWQA-UIRB is 28,358 km^2, upstream from Ottawa, Illinois, which is smaller than the UIRB as defined in this study. For the purpose of incorporating hydrologic modeling with isotopic and chemical measurements of river samples previously taken along the Illinois River, from Lockport to Peoria, and its tributaries, the main river segment from Ottawa to Peoria and associated tributary watersheds are also included as our study area. To prevent any future confusion, the term UIRB in this dissertation refers to our study area, instead of the USGS study area.

The UIRB drains a total area of 37,353 km^2, covering 38 counties in 4 states: 26 counties in northeastern Illinois (>50% of the basin area), 13 counties in northwestern Indiana, 5 counties in southeastern Wisconsin, and 1 county in southeastern Michigan (<0.1% of the basin). If tracked along the Illinois River Waterway, the reach course extends from Lockport Lock (upstream) to Peoria (downstream) (Figure 3).

The UIRB is divided into four major subbasins (Figure 3) based not only on the size of streams, but also on land use pattern: 1. The Kankakee River Subbasin: the Kankakee and its major tributary Iroquois drain the largest subbasin—35.8% of the UIRB. The predominant land use in this subbasin is agriculture, but some area has been substantially urbanized; 2. The Upper Illinois River Subbasin, drained by Illinois River and its agricultural tributaries (Aux Sable Creek, Mazon River, Vermillion River, Bureau Creek, and Senachwine Lake), which covers 31.1% of the study area; 3. The Fox River Subbasin draining 18.4% of the area, is also an admixture of urban and agricultural land; 4. The Des Plaines-Du Page-Chicago River Subbasin that drains 14.7% of the study area. It is dominated by urban land.

1.5.2. Geological setting

The climate of the UIRB is humid continental, characterized by cool, dry winters and warm, humid summers. The average annual temperature (1961-1990) ranges from 7 ℃ to 11 ℃, and the average annual precipitation (1961-1990), including liquid equivalent of snowfall, ranges from less than 81 cm to more than 96 cm. The elevation ranges from 135 m to 380 m above sea level. The entire UIRB is underlain by Precambrian granitic rocks at depths ranging from 300 m to 2,133 m below the surface, which are overlain by Cambrian sedimentary rocks, predominantly sandstone. The thickness of Cambrian formations ranges from 300 m to 1,500 m, with thinner formations mostly lying in the northern part of the basin and thicker formations in the southeastern part. Overlying the Cambrian rocks are Ordovician rocks composed mainly of limestone and dolomite, with minor sandstone and shale, having thickness ranging from 300 m (in the north and west) to 457 m (in the southeast). The uppermost bedrock units vary across the basin (USGS, 1999), except in Wisconsin, where bedrock of Ordovician and Pennsylvanian ages are not present. Five major Quaternary glacial periods shaped the land-surface features in the UIRB, resulting in the unconsolidated glacial deposits and glacial features (e.g., outwash plains, moraines, kettle lakes, drumlins) that cover most of the study area.

1.5.3. Land use

In the UIRB, the predominant land use type in all the subbasins, except the urbanized Chicago River Basin, is agriculture. Agriculture accounts for about 75% of the land use in the entire basin, and urban areas account for about 17% of land use (Figure 4). For the agricultural area, increasing demands for corn and soybeans have caused intensified cultivation of these crops, which are the two principal row crops in UIRB. About 36.9%

of the total UIRB area is planted with corn, and 21.6% with soybean, according to the cropland data of 2008 from the National Agricultural Statistics Service. In Illinois alone, 19 million of the state's 26.7 million acres farmland is used for growing crops, the majority of which are corn, soybeans, and wheat (CBMP, 2014). These practices have greatly affected water quality by intense applications of commercial fertilizers and other chemical compounds. Point sources in the Chicago area continue to be another major source of nutrients and other contaminants in the UIRB. There are about 196 wastewater treatment plants discharging wastewater to streams in the basin, and most of them locate in the greater Chicago area (USEPA, 1997). The inland area (colored in maroon) in Figure 4 overlaps the greater Chicago area yet covers a bigger area than the latter. No reach inside the inland area was included during any sampling of the Illinois River and its tributaries in this study. However, most of the wastewater treatment plants (WTP) or wastewater reclamation plants (WRP) of the UIRB locate in this area, including the five biggest WRPs of the Metropolitan Water Reclamation District (MWRD), namely Stickney, Calumet, Northside (O'Brien), Kirie, and Egan, in the order of decreasing plant size. The boundaries of the MWRD cover more than five million residents and thousands of industries of Cook County of Illinois. About 5.3 million m^3 of wastewater is generated each day within the district. These plants range in capacity from 4.5 million m^3 per day at Stickney, which is the world's largest WRP, to 0.09 million m^3 per day at Egan. The dominant land use of the inland area is urban. Although no river samples were taken from the inland area, effluent samples were collected at Stickney plant during each sampling event. The inland area plays an important role in contributing nitrogen to the UIRB, thus was included in the study as the drainage area of an inlet in the SWAT model.

1.6. Study methods

1.6.1. Dual-isotope approach

Under ideal circumstances, ^{15}N measurements can be used to identify nitrate sources because the two major sources of nitrate in many agricultural areas—fertilizer and manure—are generally distinctive in their $\delta^{15}N$ values (Kendall & McDonnell, 1998). However, variations in the $\delta^{15}N$ values of inputs and outputs of N-bearing compounds in the environment, along with isotopic fractionations associated with chemical, physical, and biological transformations of materials, have hampered the application of N isotopes for nitrate source identification and quantification. These transformations almost always result in ^{15}N enrichment of the substrate and depletion of the product (Kendall and McDonnell, 1998).

An early attempt to use natural $\delta^{15}N$ values for nitrate source identification in surface water was conducted by Kohl et al. (1971), who tried to trace contributions of fertilizer and animal waste to groundwater. This study was criticized because it overlooked the effect on isotopic signatures caused by mixture between point and non-point sources along shallow flow paths (Kendall, 1998). Moreover, it failed to consider critical reactions (such as ammonia volatilization, nitrification, and denitrification) that could have highly altered the $\delta^{15}N$ values (Hauck et al., 1972).

The application of N isotopes alone for nitrate source tracing in water often had limited success also because soil derived nitrate and fertilizer nitrate have overlapping N isotopic compositions. But a significant improvement in nitrate source tracing technique can be achieved by adding analysis of the $\delta^{18}O$ value of nitrate. The dual isotopic fingerprints of nitrate from dominant sources are distinct enough to allow separation (Chang et al. 2002;

Kendall & McDonnell, 1998), as shown in Figure 5. $\delta^{18}O$ values can be used to separate sources that have identical $\delta^{15}N$ values, such as nitrate fertilizer and atmospheric deposition; in the case where nitrate is derived from ammonium fertilizer, soil N, and manure have overlapping $\delta^{18}O$ values, $\delta^{15}N$ can be used to distinguish sources.

Analysis combining $\delta^{15}N$ and $\delta^{18}O$ values is also useful in identifying denitrification (Figure 5a), because the heavy isotopes (^{15}N, ^{18}O) of nitrate are preferentially enriched in residual nitrate during denitrification (Kendall, McDonnell, 1998; Böttcher et al., 1990), and the enrichment of both isotopes results in a slope ranging from 0.5 to 1.0 on the $\delta^{18}O$ vs. $\delta^{15}N$ plot (Kendall & McDonnell, 1998; Aravena & Robertson, 1998).

A combination of isotopic and concentration measurements (Figure 5b) can be used to study factors influencing isotopic composition and nitrogen chemistry during complicated mixing and biogeochemical reaction processes (Burn et al., 2009; Rock et al., 2006), to identify contributions of different nitrate sources (Accoe, 2008), and the transformations of nitrate in the watershed (Kendall & McDonnell, 1998; Mayer et al., 2002; Pardo et al., 2004; Hales et al., 2007).

The dual isotopic approach and measurement of nitrate concentrations have been successfully applied to investigate N behavior in many major basins, including the Mississippi River Basin and the Illinois River Basin (Panno et al., 2006, 2008; David et al., 1997; Royer and David, 2006; Mayer and Boyer, 2002).

David et al. (1997) calculated the nitrogen balance in the Camargo watershed (Urbana-Champaign, Illinois), of which 91% of the land-use is row-crop agriculture, predominantly maize and soybeans. They concluded that: 1) river nitrate concentration varied seasonally and is correlated to river flow. During extremely high flow events, nitrate concentration could be reduced as a result of dilution and a large amount of nitrogen was exported; during low flow periods, nitrate concentration was low probably due to denitrification along with lack of tile inputs. 2) Tile drainage provided most of the river nitrate load. However, when river flow was greater than 50 m^3/sec, surface runoff input was more important than tile input. 3) Both soil mineralization and fertilizer nitrogen contributed to the nitrate in tile drainage and therefore to the river export. The amount of inorganic nitrogen provided by soil mineralization was about 66% as much as the fertilizer input.

Research in the Mississippi River Basin by Chang and Kendall (2002) supported David et al. (1997) in that nitrate concentration and flux in river and discharge were positively correlated under the influence of weather among agricultural sites, exhibiting seasonal patterns, and that fertilizer and mineralized-soil nitrogen were the main contributions to the total nitrogen flux to the Gulf of Mexico.

Royer and David (2006) conducted a 12-year intensive monitoring program to study the timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois. Their result showed that tile drainage was the primary mechanism for nitrate export from the study area. Precipitation and tile drainage were considered as two driving factors in nutrient export from the Midwest to the Mississippi River. In-stream nutrient concentrations were positively correlated to runoff during late winter through spring, the same period when fertilizer applied during fall was susceptible to nitrification and loss.

Mayer and Boyer (2002) used both N and O isotopes in nitrate, combined with nitrate concentration and flux measurements, to study sources of riverine nitrate in sixteen watersheds in the northeastern U.S. Their data suggested distinct sources of nitrate from among different land-uses: In predominantly forested watersheds, riverine nitrate was almost exclusively derived from soil nitrification processes with little contribution from atmospheric deposition. In watersheds with significant agricultural and urban land use, wastewater was a major source and manure nitrate a minor source, while atmospheric and fertilizer nitrate were not as significant. They also observed positive correlations between $\delta^{15}N$ values and nitrate concentrations (r^2= 0.75), and between $\delta^{15}N$ and annual N fluxes with wastewater and manure in the watersheds (r^2=0.68), indicating the dominant sources of nitrate (50% by sewage and 20% by manure application).

Panno et al. (2008) conducted a two-year investigation to study the sources and fate of nitrate in the Illinois River. They identified three main nitrate sources: tile drainage, highly denitrified groundwater, and TWW (Treated Waste Water). Contributions from these three sources varied seasonally depending on the river discharge.

The dual-isotope approach also has application in identifying denitrification. Panno et al. (2008) concluded that most groundwater sources were denitrified because their $\delta^{18}O$ and $\delta^{15}N$ values were correlated along a trend line with a slope of 0.5. They noticed that a positive shift in isotopic values occurred in Peoria Lake in August 2005, when the Illinois River was near its record low stage. Here nitrate concentration decreased indicating a consumption zone. Using the Rayleigh distillation equation, they calculated a fractionation effect caused by in-stream benthic denitrification of about +2‰ for a NO_3-

N concentration loss of 50%. They suggested that most denitrification occurred in the soil zone and the shallow saturated zone during low flow periods.

1.6.2. SWAT (Soil and Water Assessment Tool)

SWAT is a physically based continuous time model that operates on a daily time step was developed by Dr. Jeff Arnold in the early 1990. It was developed for the USDA Agricultural Research Service (ARS) to predict “the impact of land management practices on water, sediment, and agricultural chemical yields in large, complex watersheds with varying soil, land use, and management conditions over long periods of time” (Srinivasan and van Griensven, 2005). SWAT incorporates features of several valuable USDA- Agricultural Research Service (ARS) models, which were designed in response to the Clean Water Act. Models that contributed significantly to the development of SWAT were Chemicals, Runoff, and Erosion from Agricultural Management Systems (CREAMS), Groundwater Loading Effects on Agricultural Management Systems (GLEAMS), and Erosion-Productivity Impact Calculator (EPIC) (Neitsch et al., 2009). SWAT is a direct outgrowth of Simulator for Water Resources in Rural Basins (SWARRB), a continuous time step model that was developed to simulate nonpoint source loadings from watersheds. The SWARRB model was merged with another model ROTO (Routing Outputs to Outlet) to create SWAT. ROTO was developed to combine outputs of multiple SWRRB runs and route flows through channels and reservoirs, and thus solved the issue with SWARRB that it could only be utilized for watersheds up to a few hundred square kilometers in size (Neitsch, 2009). Further information on SWAT development can be found in the SWAT Theoretical Document, version 2009.

SWAT can be applied to a variety of watershed studies. Santhi and Arnold (2001) used it to evaluate alternative management scenarios and estimate their effects in controlling pollution in the Bosque River Watershed; Arnold and Allen (1999) successfully quantified the ground water recharge process in the Midwest and eastern U.S.; Wu and Johnson (2007) applied SWAT to study hydrologic response of a Great Lakes Watershed to climatic variability; Demissie and Yan (2012) modeled the potential impacts of biofuel feedstock production in the Upper Mississippi River Basin. They studied the basin responses to changes in crop rotation, crop yields, fertilizer application rate, and soil properties. Constant updates and improvements by the development team as well as the research community have made SWAT a powerful tool for simulation and prediction.

Development and calibration of a SWAT model requires a large amount of data input and empirical parameters. Main input data include topography, stream network, land use, soil properties, agricultural operations (for example, fertilizer application, irrigation, and tillage), climate, reservoirs and ponds, point source pollution, and other parameters. Most of the data are available from different public websites in the United States, government agencies, or can be generated using GIS.

The model is constructed with the following steps (Figure 6):

—Watershed delineation: the first step identifies streams and drainage divides from digital elevation maps (DEM) using the eight-direction pour point algorithm (Jensen and Domingue, 1988; Olivera et al., 2006). Reaches are defined based on user-defined drainage areas; subbasin outlets are either added by users or automatically defined as the points immediately upstream of the confluences; subbasins are defined as the incremental drainage area of each outlet (Olivera et al. 2006). The subbasin simulation is beneficial especially when the watershed has multiple dominant land uses or soil types in different areas. The user is able to reference one subbasin to another spatially. In SWAT, every subbasin has a unique corresponding outlet, and thus a unique reach. No reach lies in more than one subbasin. Inlet point, reservoir, and point source can be edited manually by users in this step. All features generated during watershed delineation are stored in an attribute table where they have their own identification numbers.

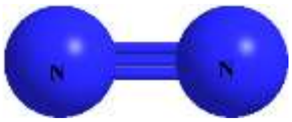
—Hydrologic Response Units (HRU) definition: grid cells are generated in each subbasin based on land use, soil type and slope. Cells that share the same soil type, land use and slope within each subbasin are grouped together and converted into polygons that represent HRUs. Each HRU has a unique combination of input data.

—Weather generation: observed weather data can be provided by users, but SWAT also includes a statistical geodatabase, which includes the locations as well as multiannual statistics of temperature, precipitation, solar radiation, and wind speed for each of the 12 months of the year for 1041 NCDC stations (Olivera et al., 2006). The weather generation module assigns one station to each subbasin based on proximity to its centroid.

—Edit SWAT input: all SWAT databases containing current model inputs are editable. Some anthropogenic elements are not built-in or subjected to changes caused by human activities, thus usually are not incorporated in model calculations. Such data include point source discharges, anthropogenic inlets, water use, and water quality. Soil chemistry, crop data, and groundwater parameters of the basin can also be manually edited in SWAT in order to match the actual conditions in the specific study area. The model management files allow users to edit or add agricultural operations, for example, fertilization timing and amount, irrigation and tillage timing, and tile drainage parameters.

FIGURES

a) Nitrogen gas, N_2



b) Nitrate (NO_3^-)

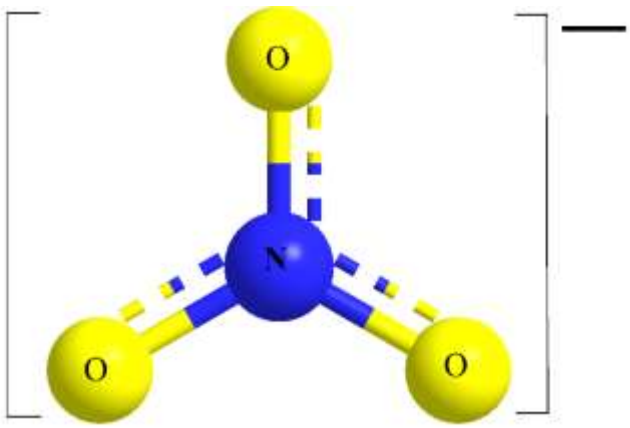


Figure 1 Molecular structures of a) nitrogen gas (N_2), and b) nitrate (NO_3^-).

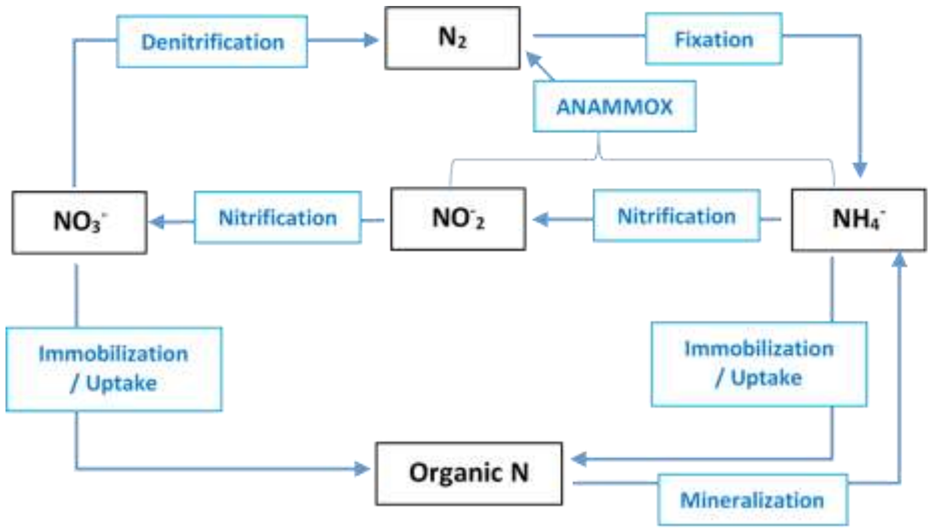


Figure 2 Major compounds and reactions in the N cycle (modified from Nestler et al., 2011).

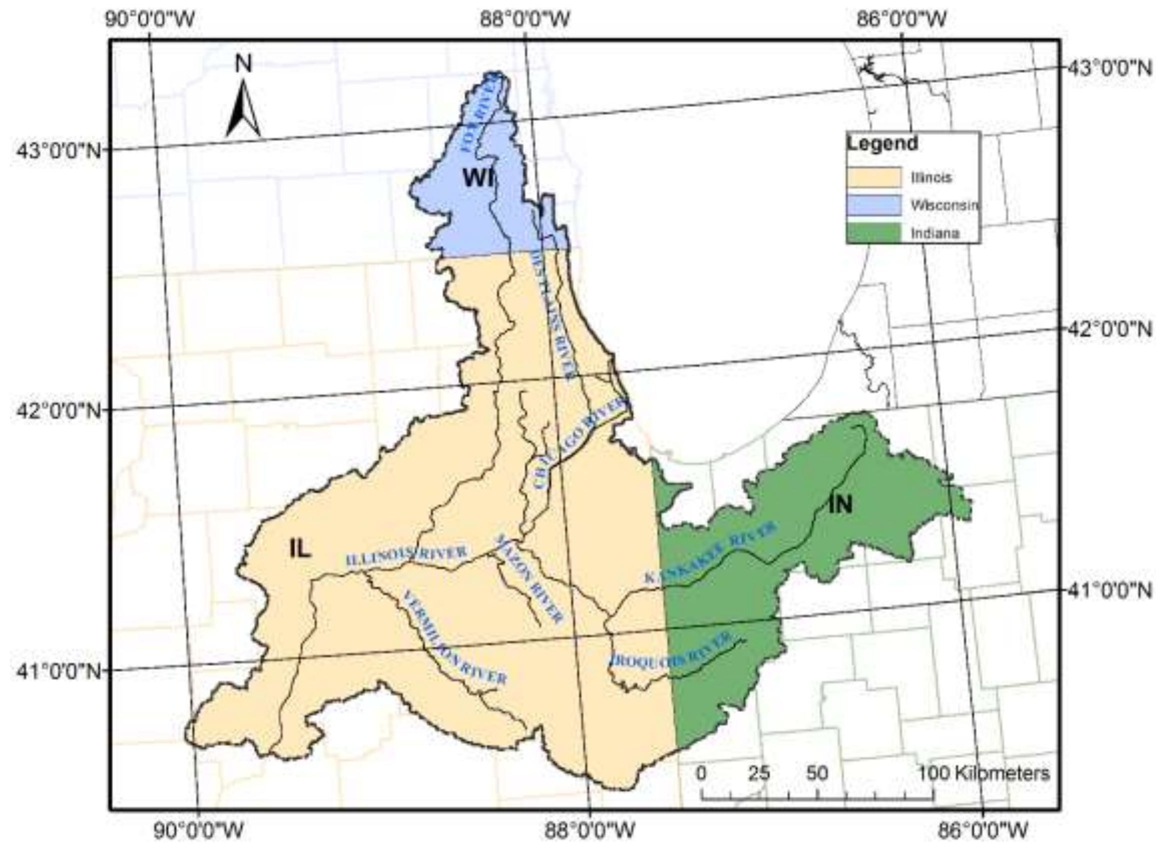


Figure 3 Upper Illinois River Basin (UIRB), location, and major tributaries. The UIRB can be divided to four major subbasins based on land use patterns and stream sizes: The Kankakee River Subbasin, The Fox River Subbasin, The Des Plaines-Du Page-Chicago River Subbasin, and The Upper Illinois River Subbasin.

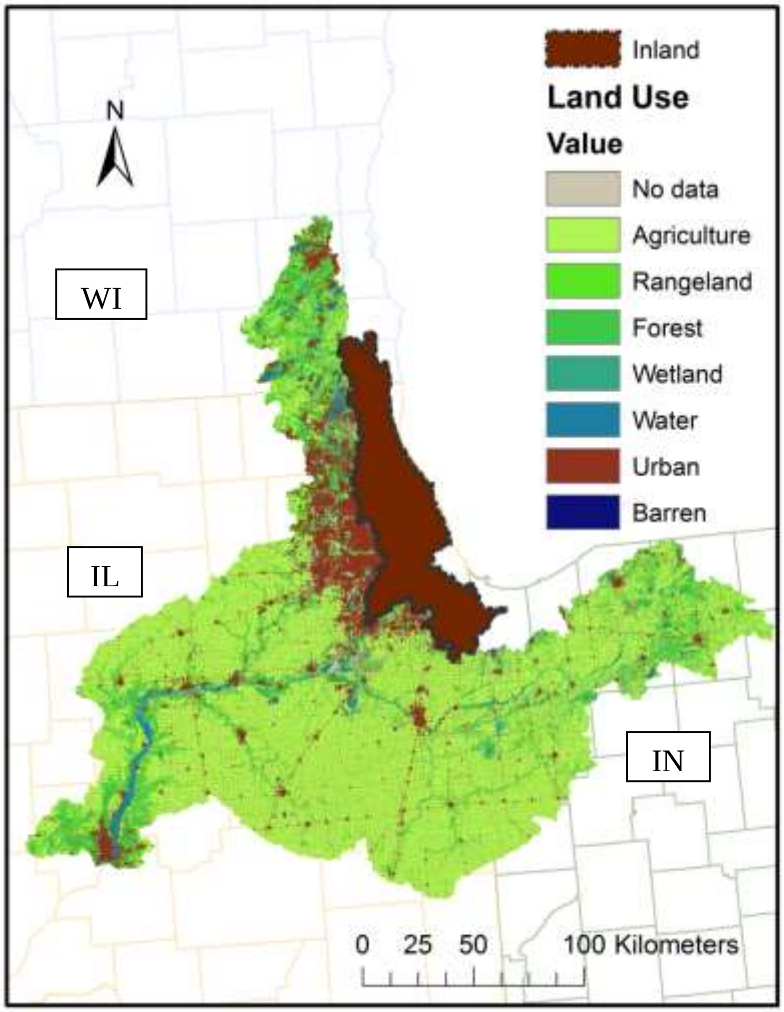
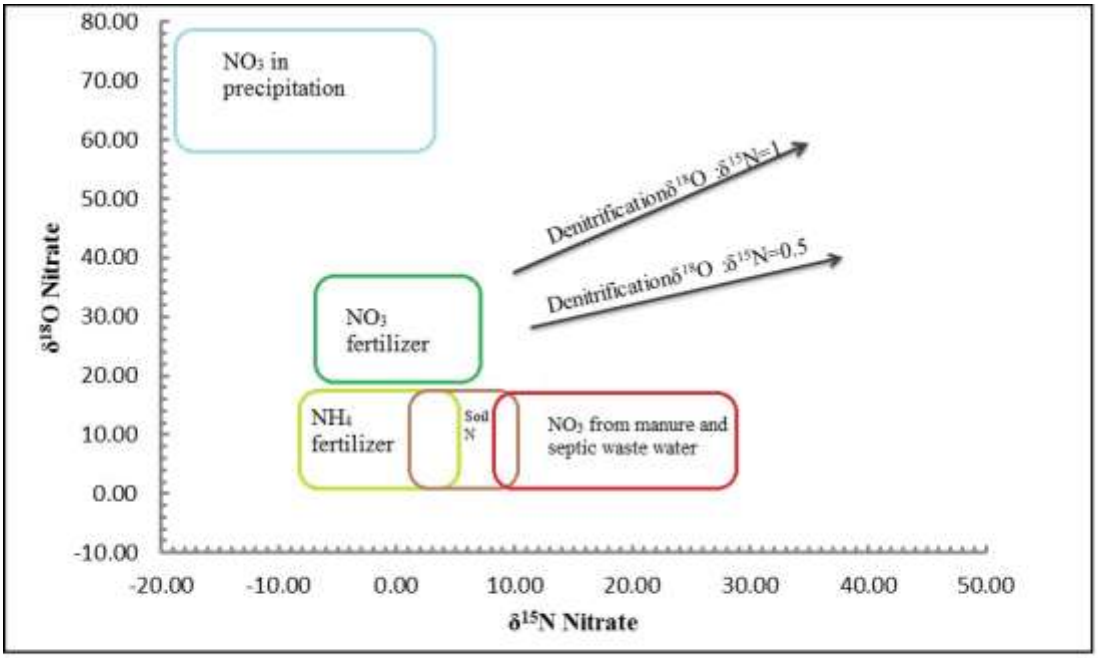


Figure 4 The distributions of land use in the UIRB, and the location of modeled inland (modified from CDL 2008, Cropland Data Layer, National Agricultural Statistics Service). The study area covers 38 counties in 4 states: IL-Illinois, WI-Wisconsin, IN-Indiana, and Michigan (< 0.1% of the basin area). 75% of the land use in the UIRB is agricultural, and urban land use accounts for about 17%. The inland area overlaps the Greater Chicago Area, where dominant land use is urban.

a)



b)

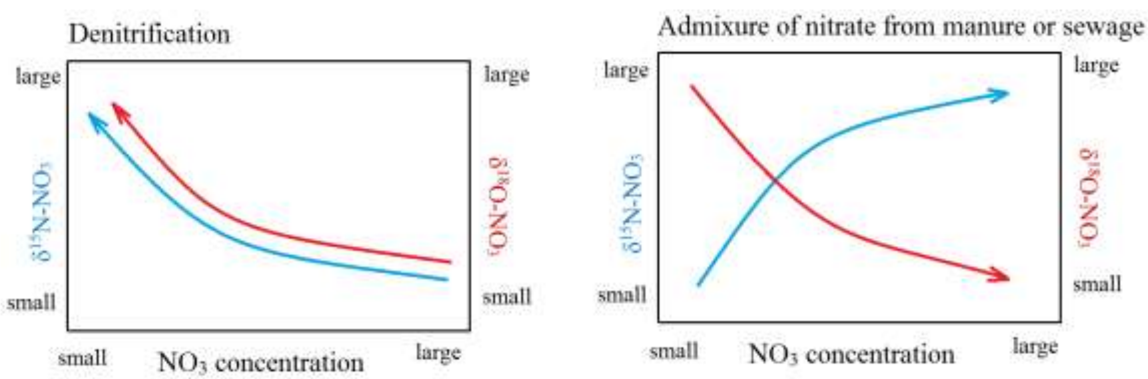


Figure 5 a) $\delta^{15}N$ and $\delta^{18}O$ (‰) values of nitrate derived from different sources (data modified from Kendall & McDonnell, 1998; Granger et al., 2008). b) Changes of concentration, and $\delta^{15}N$ and $\delta^{18}O$ (‰) values of nitrate during different processes (modified from Mayer et al., 2002). Blue lines represent changes of $\delta^{15}N$ values associated with concentration changes, and red lines represent $\delta^{18}O$ value changes in the same process. If the decrease in NO_3 concentration is accompanied by increase in both $\delta^{15}N$ and $\delta^{18}O$ values, denitrification is the dominant process in the system; if the decrease in NO_3 concentration is accompanied by increase in $\delta^{15}N$ value and decrease in $\delta^{18}O$ values, mixing between fertilizer and manure/wastewater sources is the dominant process. Lines only demonstrate trends of change, and do not represent real values.

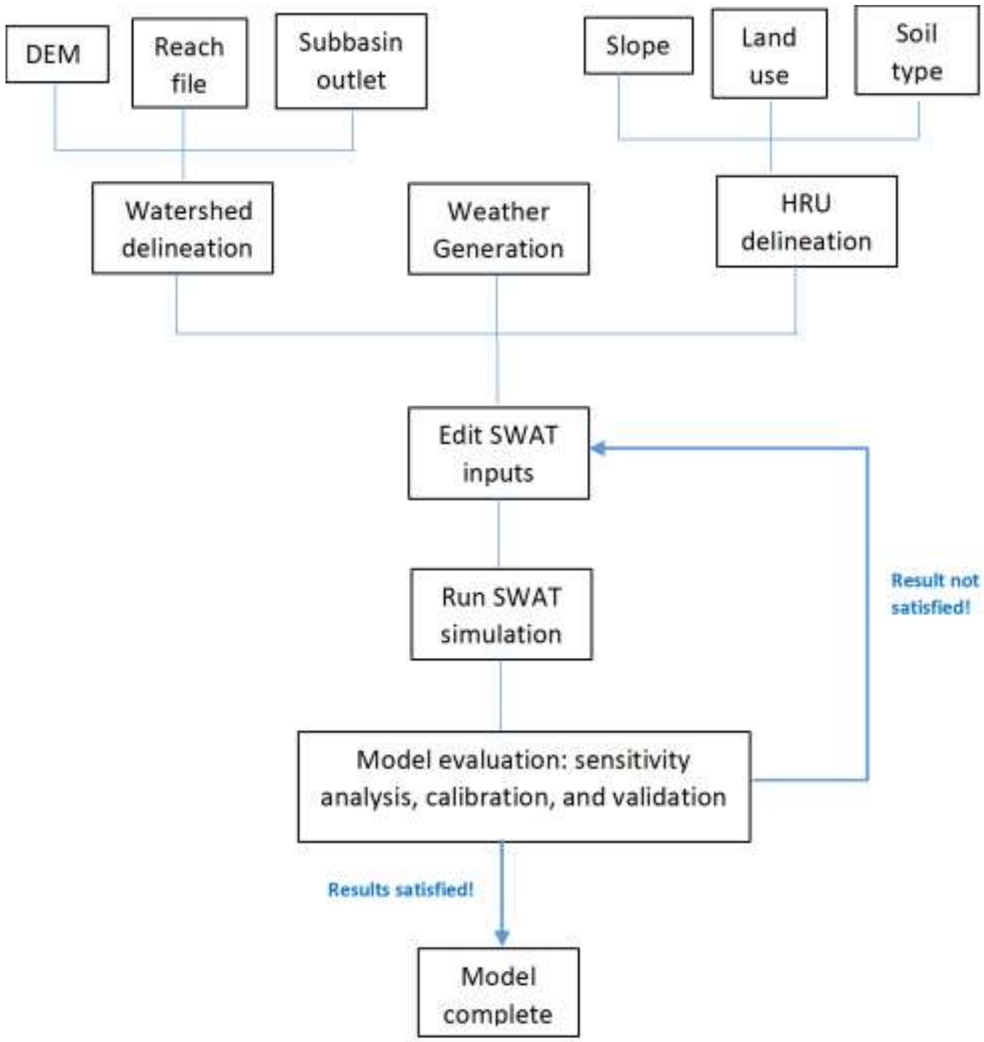


Figure 6 Flowchart of SWAT model construction, data input, and simulation. The major inputs for model construction and watershed delineation include the followings: topography data (Digital Elevation Map), reach file, weather data, land use map, slope data, and soil type. Model evaluations are carried out after initial simulation. If the results of calibration and validation are satisfactory, model is completed and ready for application; if not, further edits of SWAT inputs and parameters are required for better calibration and validation, until satisfying results are reached.

CHAPTER 2

2. SEASONAL VARIATIONS IN NITRATE FLUX AND ISOTOPIC COMPOSITION IN THE UPPER ILLINOIS RIVER BASIN

Chapter 2 will be published in future as follows with minor modification:

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2.1. Abstract

The $\delta^{15}N$ and $\delta^{18}O$ values of nitrate were measured in 400 water samples collected from the Upper Illinois River and its tributaries, including effluent from Chicago's largest wastewater treatment plant (WTP). Combining nitrate concentration and dual-isotopic measurements, we studied the influence of land use and seasonality on nitrate sources, mixing, and transformation within the Upper Illinois River Basin (UIRB) watershed. The data indicate that WTP effluent and agricultural drainage waters are the two principal nitrate endmember sources within the UIRB. Isotopic compositions indicate that the large pulse of nitrate entering streamflow during the annual spring flushing event is mostly derived from agricultural input, whereas there is a less variable year-round input from multiple WTP effluent sources. The spring samples of agricultural tributaries have nitrate isotope ratios similar to those of spring samples of tile drainage nitrate, indicating that tile drainage water is a primary nitrate source to these tributaries, and that nitrification of reduced fertilizer and mineralization of soil organic nitrogen are the dominant nitrate sources in spring for agricultural land. Isotopic compositions of nitrate in tributaries draining agricultural subbasins define an apparent denitrification trend with $\delta^{15}N$ and $\delta^{18}O$ values increasing as nitrate concentrations decrease from spring through fall. This trend is also evident in tributaries having mixed urban-agricultural land use, but less so in those dominated by urban land use where WTP effluent is the dominant source of nitrate. Precipitation and temperature have a strong impact on nitrate export by forcing nitrate transfer into streamflow and by regulating denitrification and uptake processes.

2.2. Keywords

Nitrate, isotopic composition, Illinois River, land use, denitrification

2.3. Introduction

Nitrogen (N) plays an essential role in plant growth and metabolic activities of living organisms as a key component of nucleic acids, amino acids, protein, and coenzymes (Mengel and Kirkby, 2001; Hodge, 2005; Li et al., 2013). Excess quantities of nitrate and other nutrients are introduced to the environment by human activities, causing enhancement of primary production in fresh water and marine ecosystems, leading to noxious phytoplankton blooms and bottom water hypoxia in lakes and coastal waters (Turner and Rabalais, 1994; Vitousek et al., 1997; Rabalais, 2001; Justić et al., 2003). The sources of environmental nitrate include the following: agricultural input (nonpoint sources) of nitrogen fertilizer and animal manure via tile drainage or leaching from soil; domestic or industrial nitrogen-bearing wastewater via sewage (point source); fossil fuel combustion and direct atmospheric deposition; and mineralization of soil organic nitrogen (David et al., 2010; Nestler et al., 2010). Many studies have shown that high riverine nitrate export to the Gulf of Mexico is associated with land use patterns in the Mississippi River Basin, typically from widespread cultivation of row crops such as corn and soybeans, along with substantial contributions from wastewater effluent in urban areas having high population density (David et al., 1997; Goolsby et al., 1999; Chang et al., 2002; Royer and Gentry, 2006; David et al., 2010).

The Illinois River contributes a considerable proportion (16-19%) of the total annual nitrogen flux from the Mississippi River Basin (Goolsby et al., 1999; Sullivan, 2000). Regression models indicate that the average annual flux of nitrate from the Illinois River was 113,660 metric tons per year during 1980-1996 (Goolsby et al., 1999). The Illinois River is a major tributary of the Mississippi River and flows through one of the most productive farming regions in the US. Its tributaries also flow through some of the most populated and urbanized areas in the Midwest US, including Chicago (Arnold et al., 1999; Mitsch and Day, 2006). The concentration of riverine nitrate in the Illinois River has increased substantially in the last century: the average nitrate concentration in the Upper Illinois River was 1.89 mg/L in 1896-1899, and increased to 4.24 mg/L in 1980-1996; for the Lower Illinois River, nitrate concentration increased from 1.01 mg/L in the 19th century to 4.12 mg/L by the end of the 20th century (Goolsby et al., 1999). .

It is critical to understand the sources and behavior of nitrate within the Illinois River Basin in order to help control the annual nitrate flux to the Gulf of Mexico and to preserve the quality of water and ecosystems. Identifying nitrate sources and understanding nitrogen transport mechanisms can be challenging, due to the occurrence of mixing and complex biogeochemical transformation processes, such as nitrification, fixation, mineralization, and denitrification, which are further complicated by the movement of water and sediments (Groffman et al., 2006; Alexander et al., 2009; Nestler et al., 2010). In this study we applied measurements of nitrate concentrations and dual stable isotope ratios (N, O) to identify and quantify different nitrate sources within the Upper Illinois River Basin (UIRB). We also evaluated the application of nitrate isotopic data to estimate the apparent extent of denitrification and uptake processes occurring within the watershed.

This study was a joint effort of the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC), the US Geological Survey (USGS) Reston Stable Isotope Laboratory (RSIL), and the Environmental Isotope Geochemistry Laboratory (EIGL) of the University of Illinois at Chicago (UIC). The Illinois Waterway Monitoring Project of the MWRDGC has conducted annual water quality surveys along the Illinois Waterway from the Lockport Lock (upstream) to the Peoria Lock (downstream) since 1984 to monitor water quality under the impact of the large and continuous amount of treated wastewater effluent released to the waterway in the Chicago region. Although stable isotope ratios of nitrogen and oxygen ($\delta^{15}N$ and $\delta^{18}O$) in nitrate can provide important insights into nitrate sources, denitrification, and mixing processes (Groffman et al., 2006; Panno et al. 2008; Deutsch et al., 2009; Nestler et al., 2010), they are not routinely measured during monitoring surveys. From October 2004 to December 2008, the MWRDGC surveys included a special sampling program for the nitrate isotope analyses that were conducted by our team in the Upper Illinois River and its tributaries.

2.4. The Upper Illinois River Basin (UIRB)

The UIRB drains a total area of 37,353 km^2, covering 38 counties in 4 states: 26 counties in northeastern Illinois (>50% of the basin area), 13 counties in northwestern Indiana, 5 counties in southeastern Wisconsin, and 1 county in southeastern Michigan (< 0.1% of the basin). If tracked along the Illinois Waterway, the reach course extends 214.5 km, from Lockport Lock (upstream) to Peoria (downstream). Our definition of the Upper Illinois River Basin (UIRB) differs from that of the USGS National Water-Quality Assessment (NAWQA) program (Arnold, 1999). The drainage area of the NAWQA-UIRB includes 28,358 km^2 upstream of Ottawa, Illinois (Figure 7), which is smaller than the UIRB in our study, the boundary of which is defined by the extent of our sampling area. The term UIRB used in our study refers to the area outlined in Figure 7.

The UIRB is divided into four major subbasins (Figure 7) based on stream size and land-use patterns: 1. The Kankakee River Subbasin: the Kankakee River and its major tributary (Iroquois River) drain the largest subbasin—35.8% of the UIRB. The predominant land use in this subbasin is agriculture, but some area has been urbanized; 2. The Upper Illinois River Subbasin, drained by the Illinois River and its agricultural tributaries (Aux Sable Creek, Mazon River, Vermillion River, and Bureau Creek), which drain 31.1% of the study area; 3. The Fox River Subbasin, draining 18.4% of the area, is also a mixture of urban and agricultural land use; 4. The Des Plaines-Du Page-Chicago Sanitary and Ship Canal Subbasin drains 14.7% of the study area and is dominated by urban land use.

Agricultural land use accounts for about 75% of the land area in the entire UIRB, and urban land use accounts for about 17% of land area. The land use data in Figure 8 are calculated based on the Crop Data Layer (2008) of the National Agricultural Statistics Service. The agricultural land use is a combination of all the farming regions of corn, soybean, hay, wheat, and pasture, whereas the urban land combines all urbanized area with three types of population densities (high, medium, and low) inside the UIRB. For the agricultural land area, increasing demands for corn and soybeans have caused intensified cultivation of these crops, which are the two principal row crops in the UIRB. About 36.9% of the total UIRB area is planted with corn, and 21.6% with soybeans, according to the cropland data of 2008 from the National Agricultural Statistics Service.

Point sources in the Chicago area continue to be a major source of nutrients and other contaminants in the UIRB. There are about 196 wastewater treatment plants (WTP) discharging wastewater to streams in the basin, and most of them locate in the greater Chicago area (Arnold and Ruhl, 1999). The inland area (colored in maroon) in **Figure 8** overlaps the greater Chicago area. The dominant land use of the inland area is urban. Most of the WTPs of the UIRB locate in this inland area, including the five largest WTPs of the MWRDGC, namely Stickney, Calumet, Northside (O'Brien), Kirie, and Egan, in the order of decreasing capacity. The boundaries of the MWRDGC include more than five million residents and thousands of industries of Cook County, Illinois. About 5.3 million m^3 of wastewater is generated each day within this district. All MWRDGC wastewater effluent drains into the Chicago Sanitary and Ship Canal that converges with the Des Plaines River at Lockport. The Stickney Water Reclamation Plant is the world's largest WTP, having a treatment capacity of about 4.5 million m^3 per day, thus, its effluent plays an important role in the nitrate inventory of the UIRB.

2.5. Methods—sample collection and measurement

Three separate sampling programs were conducted by MWRDGC personnel from 2004 to 2008: (1) water samples from 49 stations along the main stem of Illinois River (including segments of Chicago Sanitary and Ship Canal and Des Plaines River) with a total length of 222 km were collected in October 2004, and May, August, and October, 2005; (2) seven of these 49 stations were sampled monthly in 2006, from March to October (stations 1, 4, 8, 20, 23, 30, and 39); and, (3) In 2008, 16 locations were sampled monthly in March through October, including: seven stations on the Illinois River, and nine stations near the outlets of its major tributaries, which are Des Plaines River, Du

Page River, Kankakee River, Aux Sable Creek, Mazon River, Fox River, Vermillion River, and Bureau Creek, as well as Senachwine Lake. In addition, treated effluent samples were taken from the Stickney Water Reclamation Plant during all three sampling programs. Locating in southwest metropolitan Chicago, the Stickney plant serves 2.38 million people over an area of 673 km^2. Locations of all sampling stations are shown in Figure 8.

All river samples were collected at a depth of one meter below the surface in the center of the waterway with a submersible pump. Water was filtered on site through a 0.45 μm filter capsule during collection, sealed in a new HDPE bottle, and then chilled during transport to the laboratory where it was stored frozen until analysis of nitrate concentrations and isotopic compositions.

Nitrogen and oxygen isotope ratios of nitrate, along with nitrate concentration, were measured at the USGS Reston Stable Isotope Laboratory (RSIL) using the bacterial denitrification method (Sigman et al., 2001; Casciotti et al., 2002; Coplen et al., 2004). In the first step, He gas was flushed through vials where denitrifying bacteria were cultured to remove atmospheric O_2 and N_2O. Water samples bearing nitrate were added to the vials where the bacteria converted nitrate into N_2O. The produced N_2O was then stripped from each vial by flushing again with He gas and analyzed for N and O isotopic compositions using a Thermo Finnigan Delta Plus CF-IRMS. The measurements were carried out by analyzing samples along with solutions containing nitrate isotopic reference materials and normalizing data to reported values (Böhlke and Coplen, 1995; Böhlke et al., 2003). . Nitrogen isotope values ($\delta^{15}N$) were reported in per mil (‰)

relative to atmospheric N_2, which is defined as having a $\delta^{15}N$ value of 0 ‰. Oxygen isotope values ($\delta^{18}O$) were reported in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW). All isotope ratios were reported in the delta notation:

$$\delta_{sample} = [(R_{sample}/R_{standard}) - 1] \qquad (1)$$

where, R is the $^{15}N/^{14}N$ or $^{18}O/^{16}O$ ratio of the sample or the standard.

Concentrations of nitrate in some samples were also measured by ion chromatography, along with sulfate and chloride, using a Dionex 500 ion chromatograph calibrated with certified reference solutions. Accuracies of nitrate concentrations are within ±5 % of the value reported.

2.6. Results

2.6.1. First sampling program: 2004-2005

The first sampling program was carried out in conjunction with the MWRDGC quarterly monitoring program of the Illinois Waterway from October 2004 through October 2005. Samples were collected at 49 stations locating along the main stem of Illinois River, the Des Plaines River, and the tributary Chicago Sanitary and Ship Canal in October 2004, May 2005, August 2005, and October 2005. Chemical and isotopic data are listed along with sample locations and collection date in Appendix. The measured variations in nitrate concentration, $\delta^{15}N$-nitrate values, and $\delta^{18}O$-nitrate values for the river samples are presented in Figure 9. Data for the Stickney WTP effluent samples are also presented. May 2005 samples had a notably higher average nitrate concentration (5.7 mg/L) compared to those of October 2004 (4.5 mg/L), August 2005 (3.1 mg/L), and October

2005 (3.1 mg/L). Overall, the highest nitrate concentrations were found in the upstream portion of the river; Stickney WTP effluent samples had the highest nitrate concentrations during every sampling period. A divide in nitrate concentration can be observed in Figure 9: on the upstream side of the divide, nitrate concentrations were high at stations #1 through #10, representing the Chicago Sanitary and Ship Canal and the Des Plaines River, whereas on the downstream side of the concentration divide, samples had lower nitrate concentrations. The convergence of the Kankakee River and the Des Plaines River occurs between stations #10 and #11. Observed $\delta^{15}N$ values generally increased downstream, except in May 2005 when $\delta^{15}N$ values stayed relatively constant along the waterway. The average $\delta^{15}N$ value of all samples from May 2005 (9.3 ‰) was lower than the average values in other months (11.4 ‰ in August 2005, 10.3 ‰ in October 2005, and 11.2 ‰ in October 2004). A corresponding divide in $\delta^{18}O$ values also can be observed with relatively low upstream $\delta^{18}O$ values at stations #1 through #10 and relatively high $\delta^{18}O$ values downstream of station #10. In contrast to $\delta^{15}N$, the average $\delta^{18}O$ value of samples from May 2005 (4.4 ‰) was higher than that in other months (3.1 ‰ in August 2005, 1.5 ‰ in October 2005, and 2.6 ‰ in October 2004). The location and timing of the lowest nitrate concentrations corresponded to those of the highest $\delta^{15}N$ and $\delta^{18}O$ values.

2.6.2. Second sampling program: 2006

The second sampling program was designed to better characterize temporal and spatial variations in concentrations and isotopic compositions of nitrate, by collecting at fewer stations but on a more frequent (i.e., monthly) basis, from March to October in 2006 at a subset of seven selected stations: Chicago Sanitary and Ship Canal (#1), Des Plaines

River (#4 and #8), and Illinois River (#20, #23, #30, and #39). Sampling locations are identified in Appendix I and shown in Figure 10. Samples of Chicago Sanitary and Ship Canal and the Des Plaines River exhibited somewhat different seasonal variations than Illinois River samples. Chicago Sanitary and Ship Canal and Des Plaines River sites had variable nitrate concentrations, whereas the Illinois River sites had consistently high spring concentrations and low autumn concentrations. Correspondingly higher $\delta^{15}N$ values in three autumn months were observed at stations #1, #4, and #8. The average of all NO_3-N concentrations we measured in 2006 was 5.2 mg/L for Chicago Sanitary and Ship Canal and Des Plaines River samples, and 4.9 mg/L for Illinois River samples. The spring (March-May) average for Illinois River concentration reached 6.1 mg/L, which was higher than the 5.8 mg/L spring average of Chicago Sanitary and Ship Canal and Des Plaines River samples. For Illinois River samples, spring $\delta^{15}N$ values were consistently lower than summer and autumn values. The average $\delta^{15}N$ value of Illinois River samples was 6.4 ‰ in spring, 10.1 ‰ in summer (June-August) and 9.7 ‰ in autumn (September-October). The average $\delta^{15}N$ value of Chicago Sanitary and Ship Canal and Des Plaines River samples was also lower in spring (7.3 ‰) than in summer (9.2 ‰) and autumn (9.1 ‰). The seasonal increase in Illinois River $\delta^{15}N$ values initiated in June and extended into October, and was accompanied by an increase in $\delta^{18}O$ values. There was a general increase of $\delta^{18}O$ values with distance downstream. Seasonal variations in $\delta^{18}O$ values were observed for Chicago Sanitary and Ship Canal and Des Plaines River samples: the spring average was 5.3 ‰, summer was 1.0 ‰, and autumn was 0.16 ‰. Illinois River samples also exhibited a similar seasonal trend in $\delta^{18}O$ values: highest in spring (5.2 ‰), lower in summer (4.5 ‰), and lowest in autumn (2.9 ‰).

2.6.3. Third sampling program: 2008

The third and final sampling program of this study was designed to obtain additional information about the chemical and isotopic contributions of nitrate from the major tributaries entering the Illinois River downstream of the confluence of the Des Plaines (DP) and Kankakee Rivers, along with further characterization of temporal and spatial variations along the entire Illinois Waterway. Monthly sampling was conducted from March through October, 2008. August sampling was cancelled because of high water; two samplings were conducted in October (one early and one late). Data of samples from the main stem of the Illinois River were plotted in Figure 11a. Figure 11b includes all samples collected from tributaries and Illinois River.

For the Illinois River samples, the seasonal variations in concentration and isotope ratios exhibit similar pattern with the second sampling program (Figure 11a). A minor "spring flush" event can be observed, marked by a higher average spring concentration (4.8 mg/L) compared to summer (4.0 mg/L) and fall (3.4 mg/L). The average values of $\delta^{15}N$ increased from 8.2‰ (spring) to 9.4‰ (summer), and the average $\delta^{18}O$ values stayed the same (3.3‰). The downstream portion has higher $\delta^{18}O$ values the than upstream portion. The annual average of $\delta^{18}O$ values is 1.0‰ for the upstream portion (station #1, #4, and #8), and 3.8‰ for downstream portion (station #20, #23, #30, and #39). Upstream portion has higher $\delta^{15}N$ values in the spring (8.9‰) than downstream (7.6‰), but lower $\delta^{15}N$ values through summer and fall (8.9‰) compared to downstream samples (9.7‰).

Tributary data points are highlighted by letter sample IDs in Figure 11b and the Appendix I. In Figure 11b, three nitrate hot spots in spring and summer (represented by red and yellow colors) can be observed on the concentration plot, corresponding to tributaries: the first hot spot occurs where Aux Sable Creek (AC) and Mazon River (MR) enter the Illinois River, the second one corresponds to the entry of the Vermillion River (VR), and the third one corresponds to the entry of Bureau Creek (BC) and Senachwine Lake (SL). Three cold spots (in blue color) are also evident, corresponding to the same tributaries in fall, indicating low nitrate concentrations. It is also on these same tributaries where elevated $\delta^{18}O$ values were observed during fall, forming $\delta^{18}O$ hot spots. However, $\delta^{18}O$ values of samples of these tributaries and the Illinois River segments between them stayed relatively high at all times of year. In comparison, samples of stations DP, #1, #4, #8, and DR had lower $\delta^{18}O$ values, especially during late summer through autumn. Values of $\delta^{15}N$ exhibited a seasonal increase starting in summer. The spring average of $\delta^{15}N$ values of all samples in 2008 was 8.1 ‰, while the summer average was 9.4 ‰, and the autumn average was 10.3 ‰. Low $\delta^{15}N$ values were observed at stations #13 and #14, which corresponded to high nitrate concentrations, in spring and summer. The spring average nitrate concentration of all samples in 2008 was 5.4 mg/L, while the summer average was 5.3 mg/L, and the autumn average was 3.4 mg/L. The spring average $\delta^{18}O$ value was 4.3 ‰; the summer average was 4.4 ‰ and the autumn average was 3.9 ‰.

2.7. Discussion

This study provides additional perspectives on nitrate sources and behavior in the Upper Illinois River Basin, beyond those of earlier studies. Previously there was only one study using a relatively large dataset of isotopes to study nitrate in the Illinois River Basin, which was a two-year study conducted by Panno et al. (2008) who sampled nitrate in the Illinois River and three of its tributaries,. Our four-year study focused exclusively on nitrate in the upper Illinois River and eight tributaries, as well as treated wastewater and shallow groundwater samples, and included a larger number of sampling locations and more frequent sample collections than the previous study.

2.7.1. Seasonal variations in nitrate concentration

The "spring flush" of nitrate is observed in all three sampling programs, as indicated by the high concentrations observed during March, April, and May (Figs. 9-11). The enhanced input of nitrate is most likely derived from leaching of excess fertilizer and soil nitrate that entered the tributaries through tile drainage systems and shallow groundwater (David and Gentry, 2000; Panno et al., 2006, 2008). The downstream portion of the Upper Illinois River system (beyond the confluence of the Kankakee and Des Plaines Rivers) has higher nitrate concentration in spring than the upstream portion, whereas the converse occurs in summer and autumn. This is consistent with the higher proportion of agricultural land-use in the downstream region, as opposed to the largely urbanized land-use patterns of the Chicago metropolitan region in the upstream portion.

A strong positive correlation between discharge (m^3/sec) and daily nitrate flux (tons/day) can be observed in Figure 12, with R^2 values of 0.79 and 0.86 respectively at stations Henry (ILWW Mile 190) and Marseilles (ILWW Mile 247.5). High discharge, which mostly occurred during spring, is associated with elevated nitrate flux, and is responsible for the majority of basin nitrate output. Based on another study of ours on UIRB nitrate, spring (March-May) is responsible for 40% of nitrate export on a 10-year (1999-2008) average at the basin scale.

Royer and David (2006) monitored riverine export of nutrients from agricultural watersheds in Illinois, and discovered that discharges greater than median value were largely responsible for nutrient export from the basin, which mostly occurred from mid-January to June. Our calculation demonstrated that over 70% of nitrate export occurred during the period from January to June on a 10-year average. In 2005, which was also the driest year since 1990, the January-June period was responsible for 92% of annual basin nitrate export. Discharge decreased by over 50% from May to July in 2005, and stayed low through the end of the year, which presumably created the best condition for denitrification. There was also minimum amount of tile/agricultural input of nitrate during the low flow period.

The large output of nitrate during spring is a combined result of high stream flow, high nitrate concentration, and low denitrification extent. This could be a direct outcome of intense spring precipitation, which causes high agricultural input through tiles and high soil leaching. During the high flow periods, it is unlikely for denitrification to take place and reduce the nitrate load, so that most of the nitrate that enters streams during spring can reach the Gulf (David et al., 2010; Alexander et al., 2008). The spring flush subsides in late June and early July, and has little influence in September and October. There is limited speculation on winter (December to February) nitrate export in this study because of the lack of sample collection during periods when the waterway was partially ice-covered. A study of nitrate sources in the Mississippi River Basin by Chang et al. (2002) showed that both discharge and nitrate concentrations were low in winter, and increased in spring with low $\delta^{15}N\text{-}NO_3$ values, which was consistent with a fertilizer-soil source.

2.7.2. Seasonal variations in nitrate isotopic composition

Nitrate isotopic compositions in the Upper Illinois River Basin reflect two dominant nitrate sources: treated wastewater and agricultural fertilizer, which are identified by the characteristic isotopic compositions. Nitrate isotopic compositions also reflect seasonal changes in dominant source of nitrate responding to changes in meteorological conditions (precipitation, temperature) and agricultural practices (spreading of N fertilizer) in different months of a year. During the period from March to June, thawing of soil followed by spring rains combine to generate a large increase in agricultural nitrate flux from nitrified fertilizer and mineralized soil organic N, whereas drier and warmer conditions and extended intervals of low flow are conducive to denitrification and decreased nitrate flux in the July-November period.

The $\delta^{18}O$-NO_3 values in the upstream portion of the UIRB are lower than those in the downstream portion. The $\delta^{15}N$-NO_3 values exhibit an opposite trend in spring: the downstream portion has lower $\delta^{15}N$ values in spring than the upstream portion. Monthly data of 2008 indicate that the Des Plaines River has higher nitrate concentration compared to the Kankakee River at most times of the year except in spring, when there is a large amount of agricultural nitrate runoff from fertilizer application and soil leaching. The WTP effluent remains fairly constant upstream of the confluence of the Des Plaines River and Illinois River throughout summer and fall (Figs. 9-11), whereas discharges of nitrate from agricultural runoff and groundwater reach their minimal values in these seasons, and they dilute the Illinois River nitrate.

Nitrate derived from fertilizers and soil N is characterized by lower $\delta^{15}N$ values and higher $\delta^{18}O$ values compared to nitrate derived from WTP effluent. The high $\delta^{18}O-NO_3$ values and concentration associated with low $\delta^{15}N-NO_3$ values of the downstream portion indicate that agricultural input was the dominant source of river nitrate in spring. The WTP effluent has greater impact on river nitrate in the upstream portion, as demonstrated by relatively high $\delta^{15}N$ values and low $\delta^{18}O-NO_3$ values. The overall nitrate concentration in the Upper Illinois River is lower in summer and fall compared to spring.

The isotopic data were also used to distinguish seasonal variations in dominant in-stream processes, such as mixing and nitrate removal. The distribution of nitrate isotopic data of samples collected in May 2005 display a starkly different trend than August and October samples from 2005 (Figure 13). The spring 2005 trend indicates that a large input of agricultural tile nitrate entered the waterway and mixed with WTP effluent nitrate. The August and October samples of 2004 and 2005 show a trend consistent with the occurrence of denitrification during low flow, which causes disproportional enrichment of ^{18}O and ^{15}N in the residual nitrate (Kendall and McDonnell, 1998), resulting in data arrays along a line with a slope between the 0.5 and 1.0 interval (Figure 13a).

The $\delta^{18}O-NO_3$ and $\delta^{15}N-NO_3$ values of all samples collected in three sampling programs are plotted together in Figure 13b. Groundwater samples collected from shallow wells in agricultural land at Hennepin in 2004 and 2005 are also plotted, which represent the unaltered end member of agricultural tributaries. Nitrate isotopic values of the agricultural groundwater samples show many similarities with spring tile samples, and can be viewed as an anchor point for the denitrification trajectory of agricultural tributaries. The denitrification trend can also be observed in tributaries with mixed land use, but it is not so obvious in urban stream samples (Figure 13b).

Samples with improved resolution of tributary contributions were collected monthly in 2008 to further refine our understanding of seasonal variations of nitrate isotopic compositions and individual watershed characteristics.

The spring nitrate isotope ratios of agricultural tributary samples resemble a mixture of soil N and nitrified fertilizer (Figure 14). The isotope ratios also indicate that the dominant type of fertilizer that contributes to riverine nitrate in UIRB is reduced-N fertilizer, which is consistant with the estimation made by Beaumont (2003) that the majority (85%) of synthetic fertilizer applied in Illinois was anhydrous NH_3. After application, NH_4 in the soil is subject to nitrification and leaching to surface water, groundwater, and the tile drainage system. Average values of nitrate isotope ratios of measured tile drainage water from other studies (Panno, 2006; Kelley, 2013; Smith, 2010) are also plotted in Figure 14. These measured tile $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$ values are consistent with reported values for nitrified NH_4 fertilizer and mineralized soil organic nitrogen (Kelley, 2014; Chang, 2002; Kendall, 1995, 2007; Vitoria 2004). The spring samples of agricultural tributaries have nitrate isotope ratios similar to the spring tile data, indicating that nitrification of reduced fertilizer and mineralization of soil organic nitrogen are dominant springtime processes affecting nitrate isotopic composition in agricultural land, and that tile drains are the primary path for agricultural nitrate to enter tributaries.

Wastewater treatment plant effluent has an apparent influence on tributaries with urban or mixed land uses, which have nitrate isotopic ratios similar to those of SWRP (Stickney) data in Figure 14. Mixing of urban wastewater and agricultural input is the dominant process in spring that contributes to the nitrate in the main stem of the Illinois River, while denitrification is the dominant process in summer and fall in the agricultural tributaries, as indicated by the evolving of $\delta^{18}O$ and $\delta^{15}N$ values along the denitrification trajectories. The impact of agricultural input on Illinois River nitrate diminishes through summer to fall, while WTP effluent apparently becomes the predominant nitrate source of the Illinois River in fall.

2.7.3. Influence of land-use on nitrate isotopic composition

The impact of tributary land use on the nitrate concentration is substantial, and is reflected in the nitrate isotopic compositions. Figure 14 exhibits data from the third sampling program (2008) when monthly samples were taken from major tributaries and the Illinois Waterway main stem.

The Kankakee and Fox River Subbasins are mixtures of agriculture and urban land use, and nitrate isotope data are represented by squares in Figure 14. The Des Plaines-Du Page- Chicago Sanitary and Ship Canal Subbasin is dominated by urban land use, and is represented by diamonds in Figure 14. The Upper Illinois River Subbasin (including the tributaries Aux Sable Creek, Mazon River, Vermillion River, Bureau Creek, and Senachwine Lake) has predominantly agricultural land and is represented by triangles in Figure 14. Tile drainage and SWRP data are also plotted in Figure 14. The isotopic signatures of nitrate from agricultural tributaries and WTP effluent are distinct; there is no overlap between these two end-member sources. This distinction is retained during and after denitrification. Agricultural tributary samples have a wide range of $\delta^{15}N$-NO_3 values (4.3 to 15.6‰, with average of 9.0‰) and relatively high $\delta^{18}O$ values (average 6.5‰). The O and N enrichment factor for denitrification is 0.79, within the expected interval of 0.5 to 1 (Figure 14, autumn plot). The denitrification pattern is not observed on tributary samples with urban land use (diamonds), which have nitrate with relatively high $\delta^{15}N$ values (average 10.2‰) and low $\delta^{18}O$ values (average 2.0‰). In the urban streams, the effect of denitrification is masked by the constant large nitrate input from municipal wastewater treatment plant effluents, which is the major source of nitrate in these tributaries.

Waterway samples that are geographically close to the SWRP also exhibit similar nitrate isotopic compositions to SWRP effluent, having an average $\delta^{15}N$ value of 9.1‰ and $\delta^{18}O$ value of 0.36‰, indicating the significant influence of wastewater on urban tributaries. The intermediate position of nitrate isotopic data of tributary samples with mixed land use (squares) is caused by admixture of wastewater treatment plant effluent and agriculture-derived nitrate.

The nitrate isotopic compositions of main stem Illinois River samples on Figure 14 show that Illinois River has mixed sources of nitrate. The main stem samples having similar isotopic signatures to the SWRP effluent were taken from the river section between Des Plaines River and Du Page River, where the SWRP effluent has a significant influence on the riverine nitrate content and the watershed land use is predominantly urban, whereas downstream portions of the Illinois River have nitrate isotopic compositions more closely resembling those of predominantly agricultural tributaries. The average $\delta^{15}N$ of the mixed land use samples is 9.7‰ and that for $\delta^{18}O$ is 5.1‰, while for Illinois River samples, these two values are 8.9‰ and 2.6‰ respectively.

Nitrate yield (NO_3-N kg/ km^2• Mon) from the major tributaries and two sampling locations on the Illinois River (Marseilles and Henry) in April and September were calculated in Table 1, as well as the ratios of autumn (September) to spring (April) nitrate yield. Urban watershed (Du Page River) has more constant nitrate input in both seasons, compared to agricultural watersheds (Aux Sable Creek, Mazon River, Vermillion River, and Bureau Creek). The autumn nitrate yields of the agricultural tributaries were all less than 10% of their spring nitrate yields. The intense spring precipitation and fertilizer application result in enhanced nitrate input to the river via surface runoff and tile drainage in March and April. The rapid decrease in nitrate yield of agricultural watersheds in September is a combined result of lack of direct surface input (fertilizer), enhanced plant uptake, and denitrification. Denitrification occurs mainly in benthic sediment (Böhlke, 2009). A longer residence time caused by lower discharge and stream velocity in fall allows longer reaction time of nitrate with organic-rich sediment in the stream. Tile water that has low nitrate content also contributed to the low nitrate yield in agricultural watershed. Panno et al. (2008) studied the seasonality of denitrification in drain tile water in Illinois, and concluded that denitrification was high when water level was low (fall) and slow movement of NO_3^- elongated the residence time for denitrification.

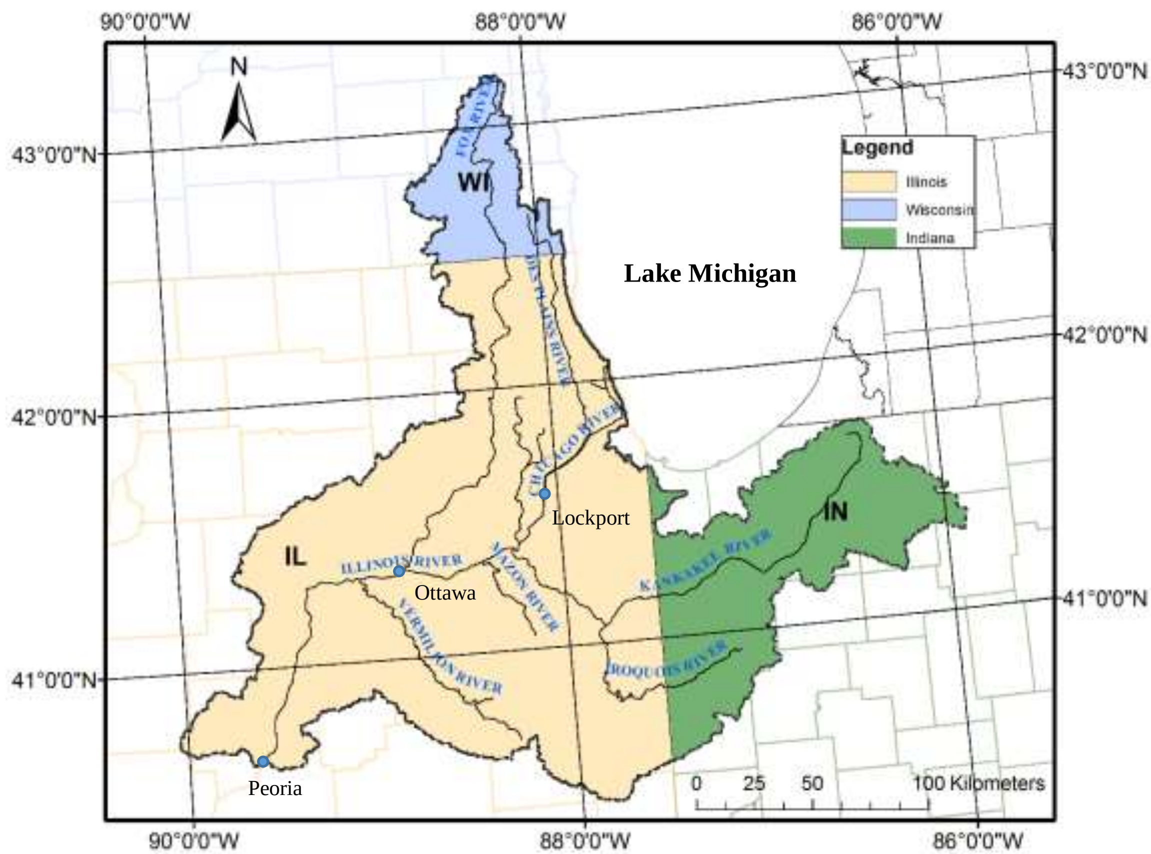
Urban watersheds do not exhibit apparent seasonal variations in nitrate yield, with the WTP effluent as the dominant nitrate source, which is a function of urban population and much less affected by diluted tile input and in-stream denitrification. Watersheds with mixed land use are also less influenced seasonally, as shown by the 0.14 autumn/spring nitrate flux ratio of the Kankakee River, and the 0.31 autmun/spring nitrate flux ratio of the Fox River (Table 1).

2.8. Conclusions

The measurements of nitrate concentrations and isotopic compositions in river water are useful indicators of nitrate sources, mixing mechanisms, in-stream processes, and the impact of land use on nitrate export. Our study demonstrated that isotopic composition of nitrate is a function of location, land use, and season. The influence of wastewater treatment plants, tributary inputs, and agricultural land use on nitrate concentrations and isotopic compositions in the Upper Illinois River are well documented, and could be used in a quantitative watershed model for future nitrate-control management. The nitrate isotope ratios indicated the dominant source of nitrate in the upstream portion of the Upper Illinois River Basin, above the confluence of the Des Plaines and Kankakee Rivers, is wastewater treatment plant effluent. Downstream of this confluence, the dominant sources of nitrate are nitrified fertilizer and mineralized soil N. The flux of agricultural nitrate became much higher in spring. Denitrification was a dominant process during low flow periods starting in summer (July) and extending to autumn (October), mainly observed in agricultural tributaries. Weather conditions such as precipitation and temperature have great impact on nitrate export, by directly affecting nitrate input and in-stream processes.

FIGURES

a):


90°0'0"W
88°0'0"W
86°0'0"W
43°0'0"N
42°0'0"N
41°0'0"N
N
Legend
Illinois
Wisconsin
Indiana
WI
IL
IN
Lake Michigan
DES PLAINES RIVER
CHICAGO RIVER
ILLINOIS RIVER
MAZON RIVER
VERMILION RIVER
KANKAKEE RIVER
IROQUOIS RIVER
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Ottawa
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0 25 50 100 Kilometers

b):

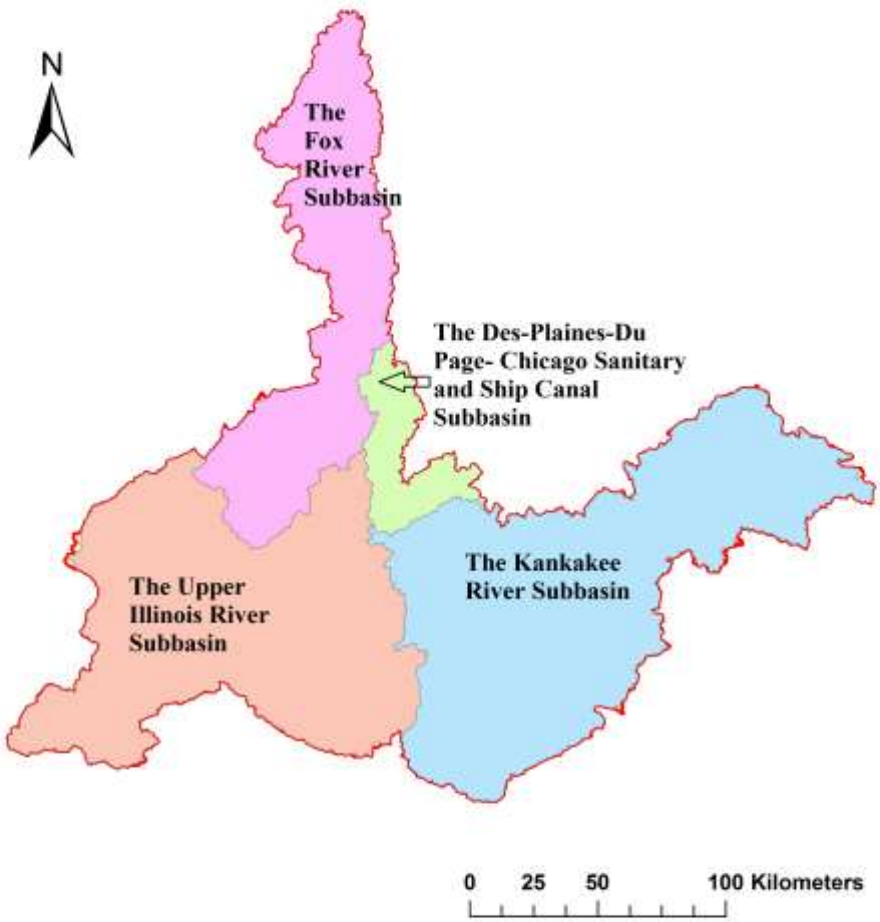


Figure 7 a): The location of the Upper Illinois River Basin and its major tributaries. b): The UIRB is divided into four major subbasins based on land use patterns and sizes of streams: 1. The Kankakee River Subbasin; 2. The Upper Illinois River Subbasin; 3. The Fox River Subbasin; 4. The Des-Plaines-Du Page- Chicago Sanitary and Ship Canal Subbasin.

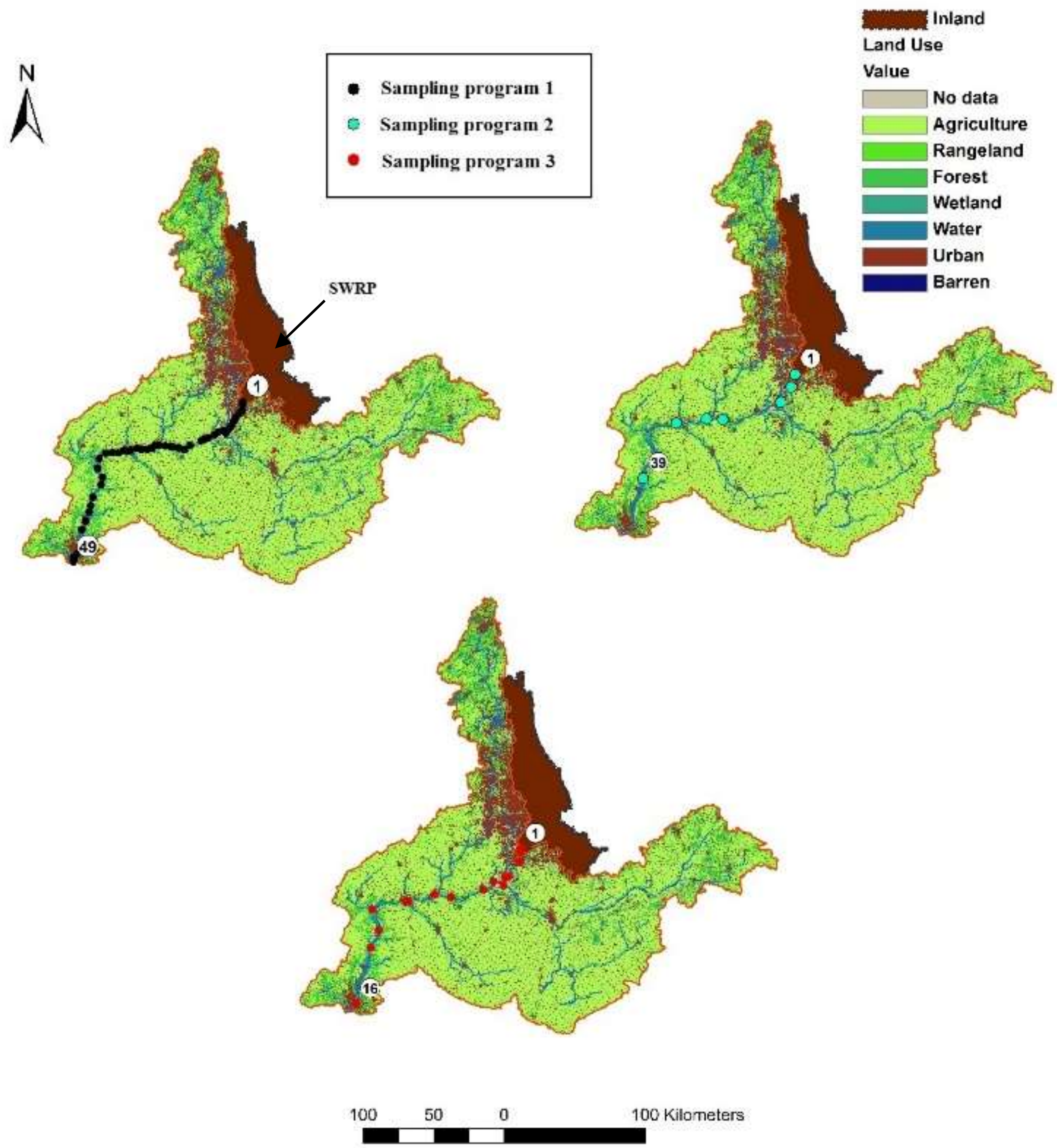


Figure 8 The distributions of land use in the UIRB and sampling locations during 3 sampling programs. Sampling program 1(black dots): Samples at 49 stations on Illinois River and its tributaries, Chicago Sanitary and Ship Canal and Des Plaines River were collected in October 2004, and May, August, and October, 2005 (black and light blue dots in left-hand figure). Sampling program 2: 7 of the 49 stations from program 1 (station #1, #4, #8, #20, #23, #30, and # 39) were sampled again in 2006 on a monthly routine, from March to October (light blue dots). Sampling program 3 (red dots): Samples were collected at the 7 stations from program 2, and 9 stations on tributaries in 2008, from March to September (no sampling in August). The inland area and location of SWRP are also shown on the map. (Land use map is modified from CDL 2008, Cropland Data Layer, National Agricultural Statistics Service).

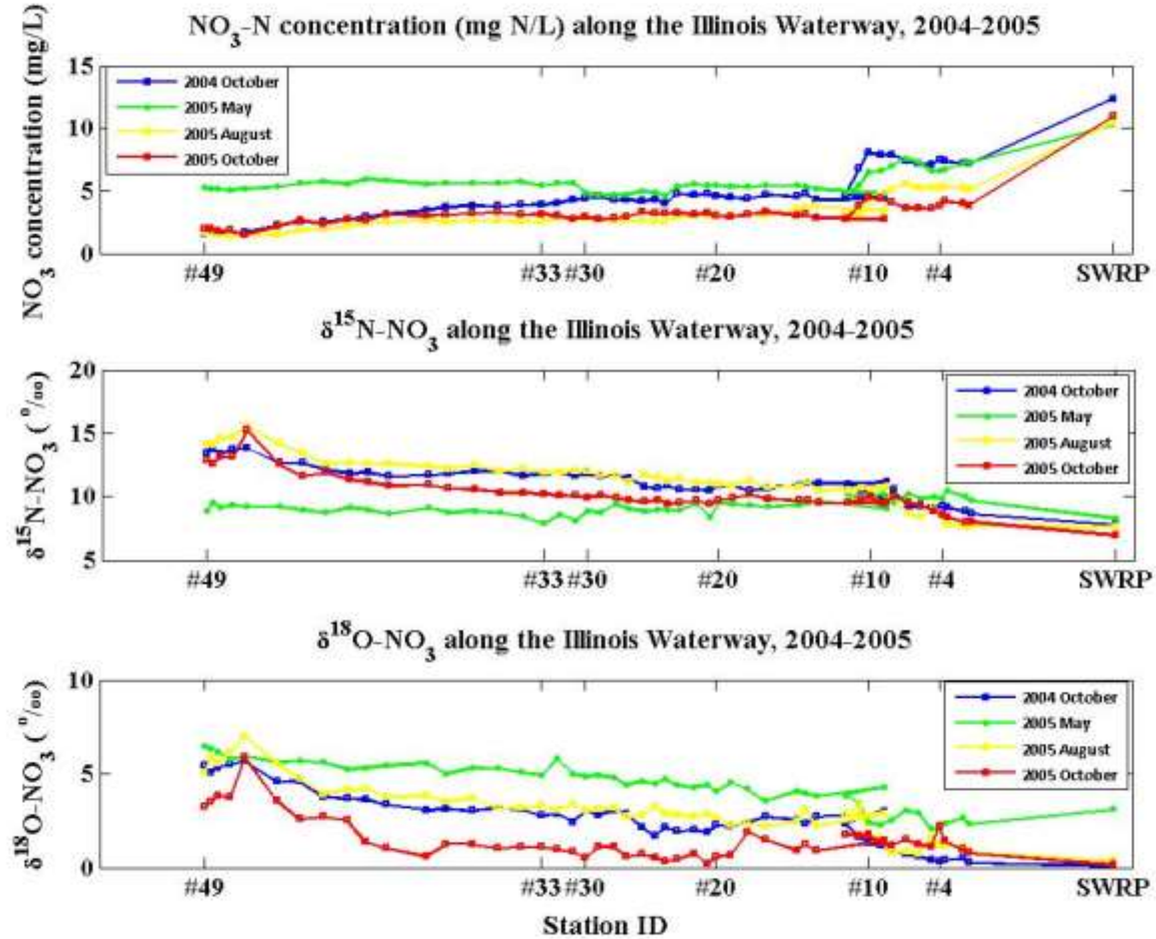


Figure 9 Sampling program 1: NO_3-N concentration, δ^{15}N values, and δ^{18}O values along Illinois Waterway (including Chicago Sanitary and Ship Canal and Des Plaines River) and SWRP, in October 2004, May 2005, August 2005, and October 2005. A divide in nitrate concentration, δ^{15}N values, and δ^{18}O values can be observed close to stations #10 and 11, where the confluence of the Des Plaines River and the Kankakee River forms the Illinois River. Sample locations are identified in Appendix.

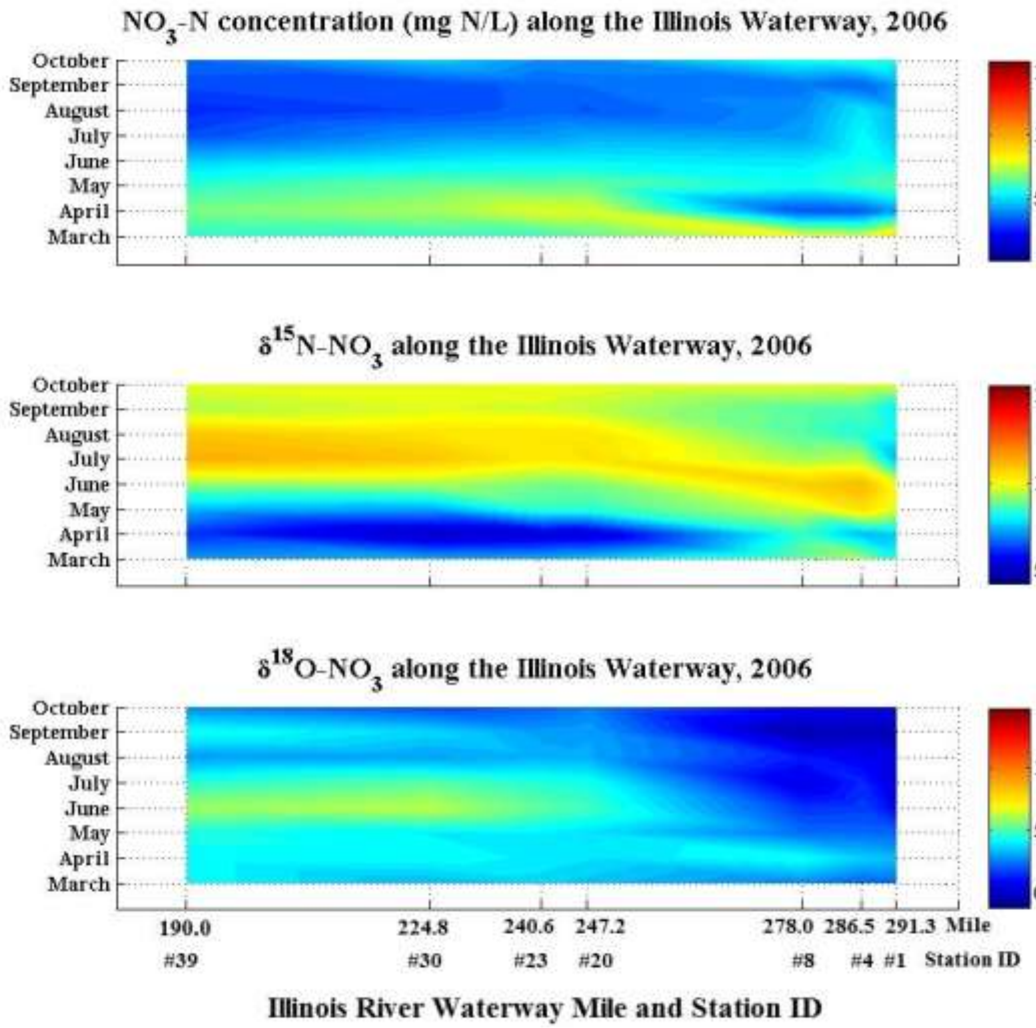
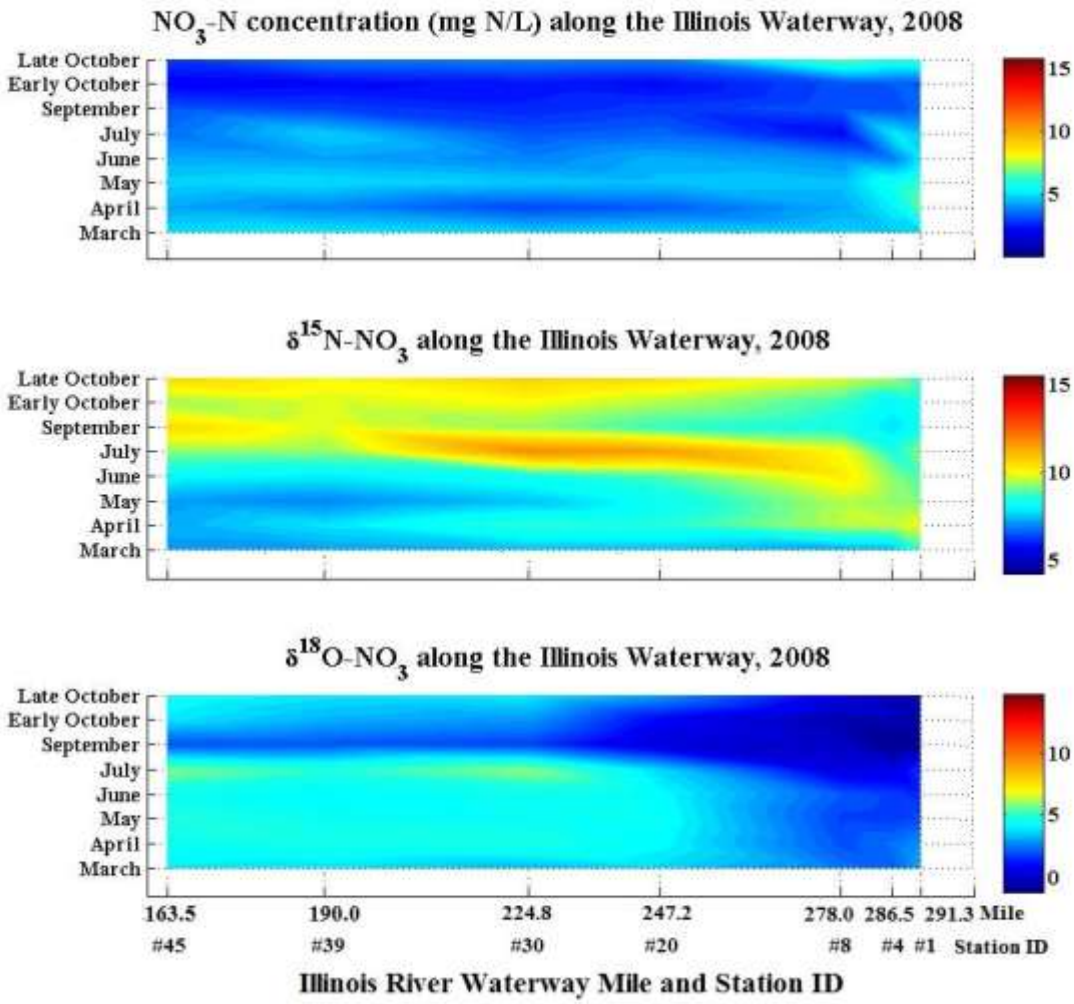


Figure 10 Sampling program 2: NO_3-N concentration, $\delta^{15}N$ values (‰), and $\delta^{18}O$ values (‰) of 7 stations on the main stem of Illinois River (including Chicago Sanitary and Ship Canal and Des Plaines River), March to October, 2006. The x-axis ticks label the Illinois River waterway miles where samples were collected. Left side (190.0 ILWW mile) is the downstream part, and right side (291.3 ILWW mile) is the upstream part. Seasonal variations in nitrate concentration and isotope ratios can be observed. The high spring concentration at middle- to down- stream portion is caused by enhanced agricultural input, which is also proved by low $\delta^{15}N$ values. The increase in $\delta^{15}N$ values and $\delta^{18}O$ values from June to October is caused by denitrification during low flow period. Upstream portion (urban land) is not apparently affected by denitrification.

a):



NO3-N concentration (mg N/L) along the Illinois Waterway, 2008
δ15N-NO3 along the Illinois Waterway, 2008
δ18O-NO3 along the Illinois Waterway, 2008
Late October
Early October
September
July
June
May
April
March
15
10
5
0
163.5 190.0 224.8 247.2 278.0 286.5 291.3 Mile
#45 #39 #30 #20 #8 #4 #1 Station ID
Illinois River Waterway Mile and Station ID

b):

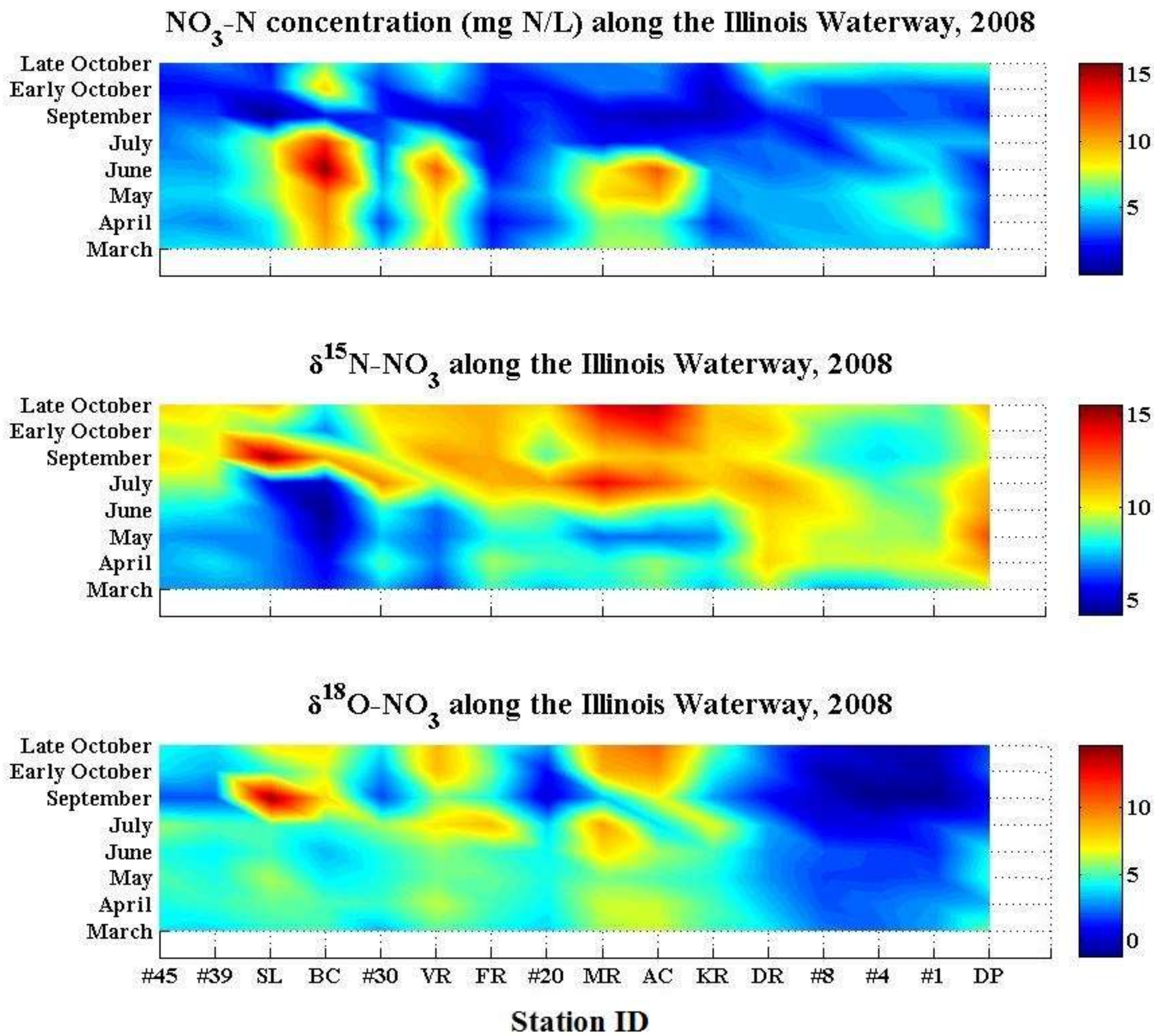
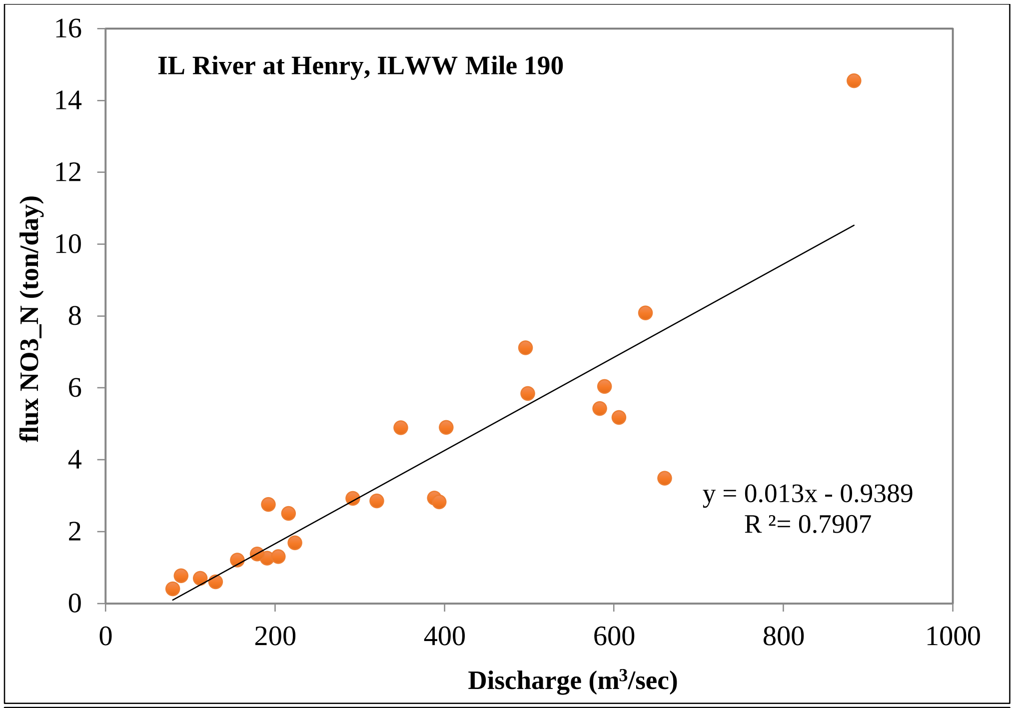


Figure 11 Sampling program 3. Samples were collected monthly from March through October, 2008. Scale bars on the right side are the same as Figure 10. a): NO_3-N concentration, $\delta^{15}N$ values (‰), and $\delta^{18}O$ values (‰) of 7 stations on the main stem of Illinois River. The x-axis ticks label the Illinois River waterway miles where samples were collected. Left side (163.5 ILWW Mile) is the downstream part (west), and right side (291.3 ILWW mile) is the upstream part (east). A minor "spring flush" is indicated by the relatively higher concentration from March to May. Indicated by low $\delta^{15}N$ values, the dominant source of nitrate of Illinois River from March to May is agricultural input, which is mixed with urban WRP effluents that have higher $\delta^{15}N$ values. Denitrification initiates in late summer (June and July) and extends to fall, as shown by elevated $\delta^{15}N$ values and $\delta^{18}O$ values. b): NO_3-N concentration, $\delta^{15}N$ values (‰), and $\delta^{18}O$ values (‰) of all 16 stations, including tributaries, which are highlighted in letter ID. The x-axis ticks label station ID, and is not proportional to the real distance along the waterway. Agricultural tributaries cause hot spots of high nitrate concentration in springtime. Same

locations are responsible for increase in $\delta^{15}N$ and $\delta^{18}O$ values over summer and fall, which is accompanied by rapid decrease in nitrate concentration.



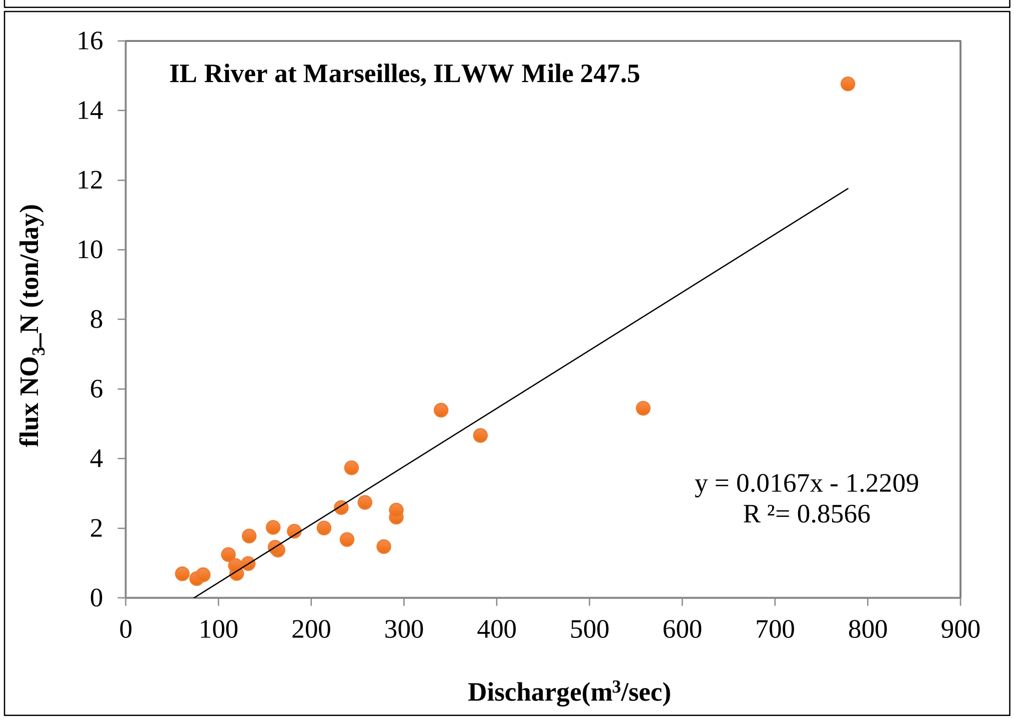
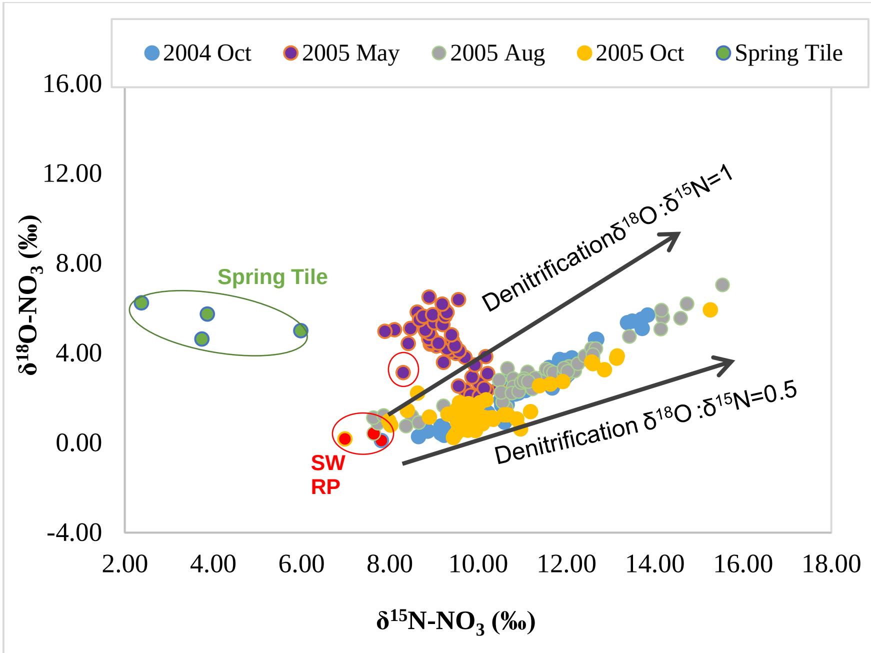


Figure 12 Daily stream discharge and daily nitrate flux of the IL River on the sampling dates. Data of samples collected at stations Henry and Marseilles during three sampling programs are plotted. A positive correlation can be observed at both locations, with R^2 values of 0.79 and 0.86 respectively. Increase in stream discharge can lead to increase in nitrate export.

a):



b):

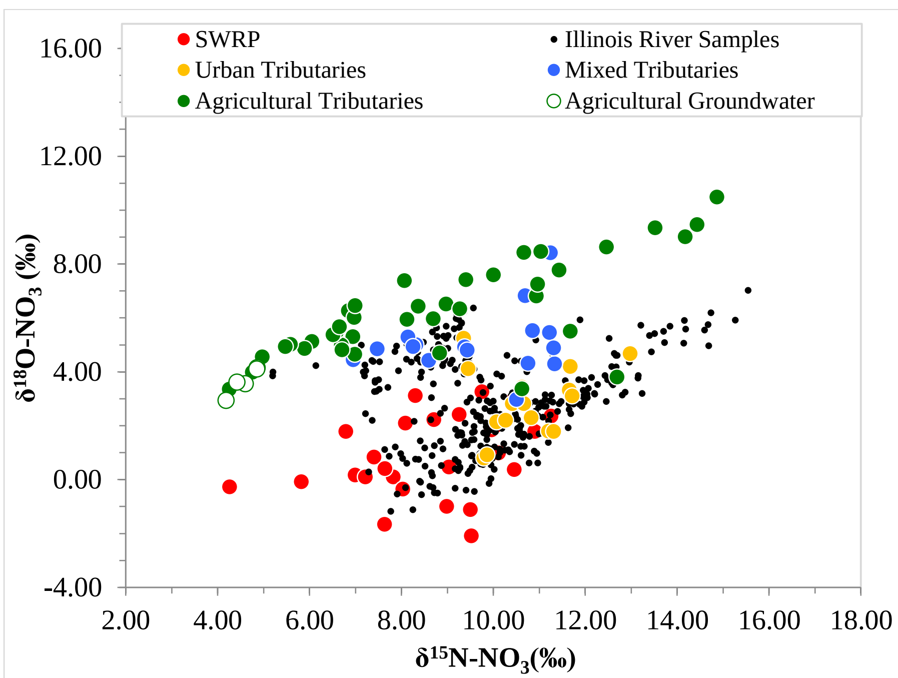
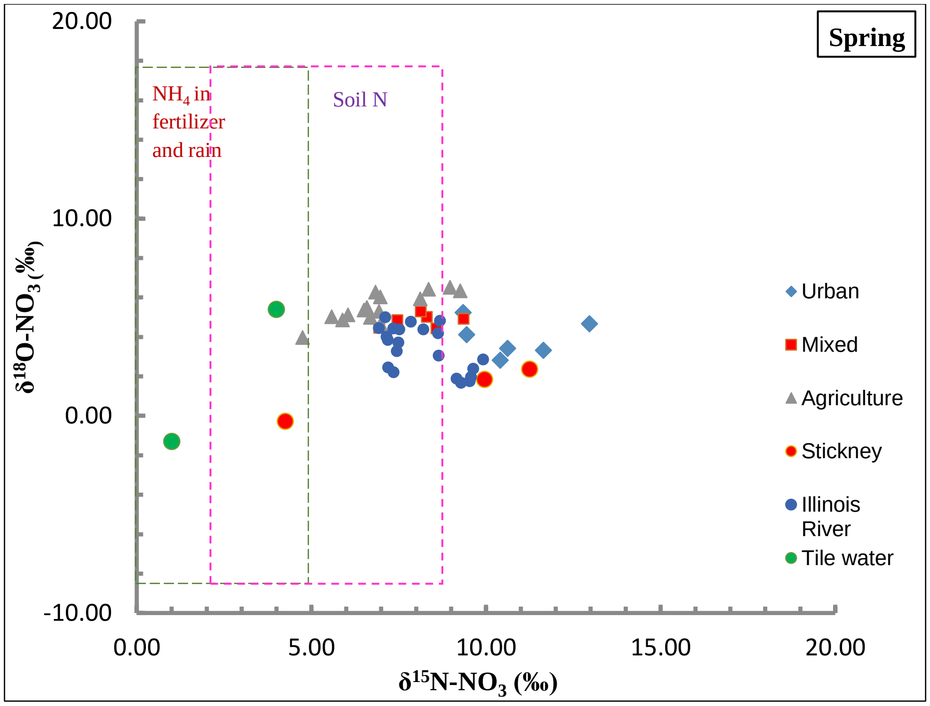
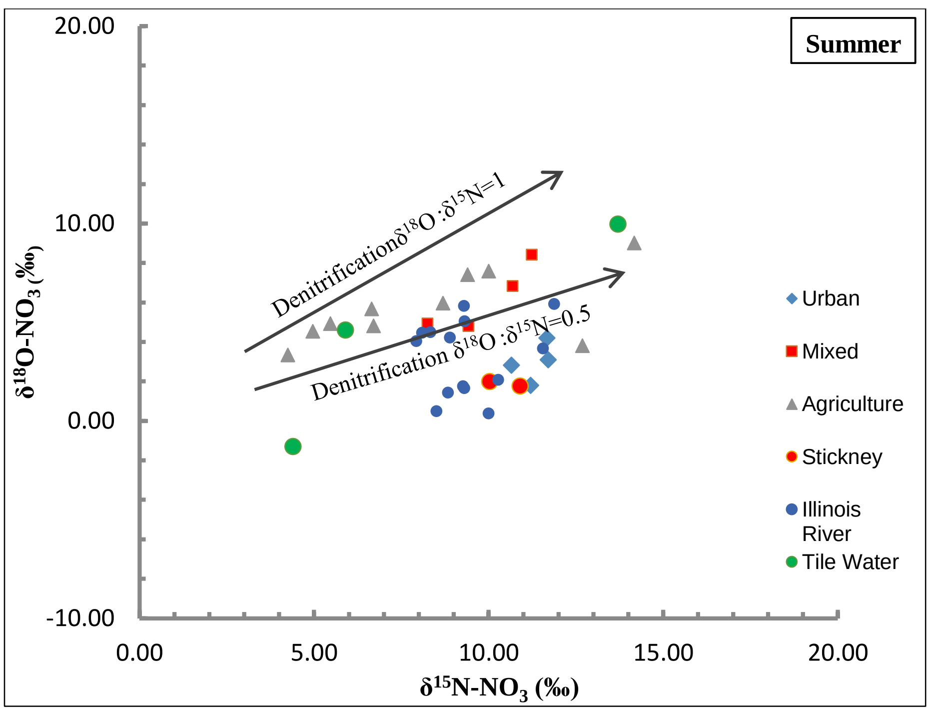


Figure 13 a): δ^{18}O-NO_3 vs. δ^{15}N-NO_3 values of various nitrate sources compared with the isotopic compositions of the sample sets collected during quarterly sampling from October 2004 to October 2005 from 49 stations along Upper Illinois River. Spring tile system data are from Panno et al. (2008). Arrows represent denitrification trends (Kendall, 1998; Granger et al., 2008). Spring samples (purple) display different trend than summer and fall samples. b): $\delta^{18}O$-NO_3 vs. $\delta^{15}N$-NO_3 values of all the sample sets collected from 2004 to 2008. Besides SWRP and stream samples, agricultural groundwater samples (white circles) collected from Hennepin are also plotted, which represent the unaltered (pre-denitrification) agricultural source. Denitrification is observed in agricultural tributary samples, but little or none is observed in urban or mixed tributary samples. Nitrate in Illinois River is a mixture between agricultural input and wastewater effluent source.


Spring
NH4 in fertilizer and rain
Soil N
δ18O-NO3 (‰)
δ15N-NO3 (‰)
20.00
10.00
0.00
-10.00
0.00
5.00
10.00
15.00
20.00
Urban
Mixed
Agriculture
Stickney
Illinois River
Tile water


Summer
Denitrification δ18O :δ15N=1
Denitrification δ18O :δ15N=0.5
δ18O-NO3 (‰)
δ15N-NO3 (‰)
20.00
10.00
0.00
-10.00
0.00
5.00
10.00
15.00
20.00
Urban
Mixed
Agriculture
Stickney
Illinois River
Tile Water

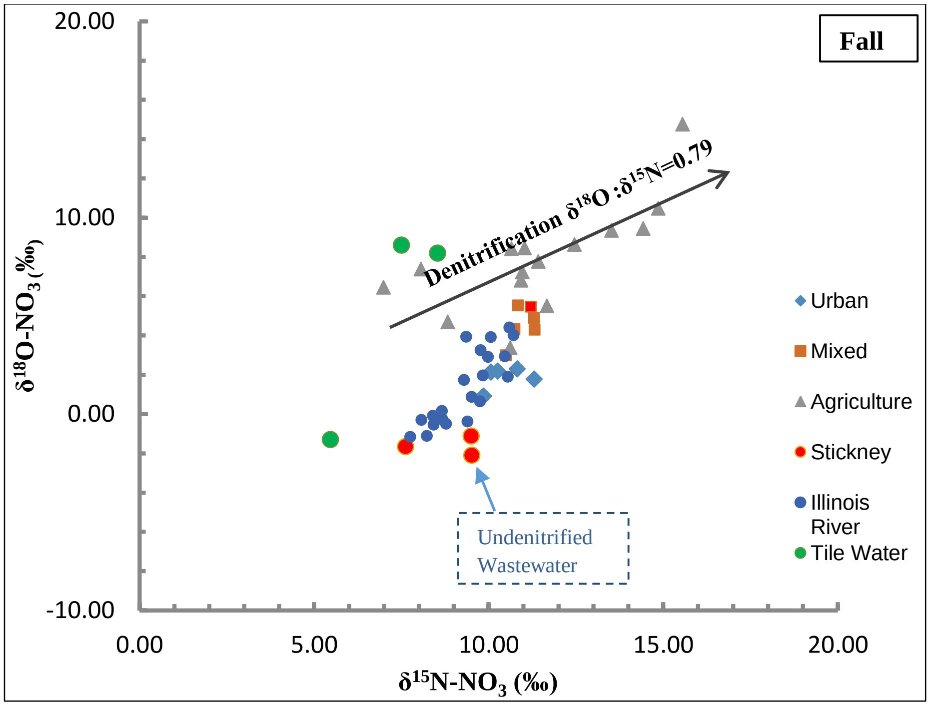


Figure 14 $\delta^{18}O$-NO_3 vs. $\delta^{15}N$-NO_3 of all monthly samples from 16 monitoring stations (IL River and tributaries) and SWRP, in spring (March to May), summer (June to August), and fall (September to late October), 2008. Vectors indicate reported denitrification trajectories that may describe much of the variations. Boxes in the spring plot represent the typical ranges of NH_4 fertilizer and soil N sources of nitrate. The dominant contribution of spring nitrate is the mixture of mineralized soil N and nitrified NH_4 fertilizer. Summer and fall are controlled by mixing of two end members: undenitrified SWRP effluents and denitrified agricultural tile water. Denitrification starts in late summer, as indicated by the agricultural tributary samples. Averaged values of nitrate isotope ratios of drain tile water from other studies are also plotted: spring tile—Panno (2008) & Kelley (2013); summer—Panno (2006), Kelly (2013), and Smith (2011); fall—Panno (2006), Kelly (2013), and Smith (2011).

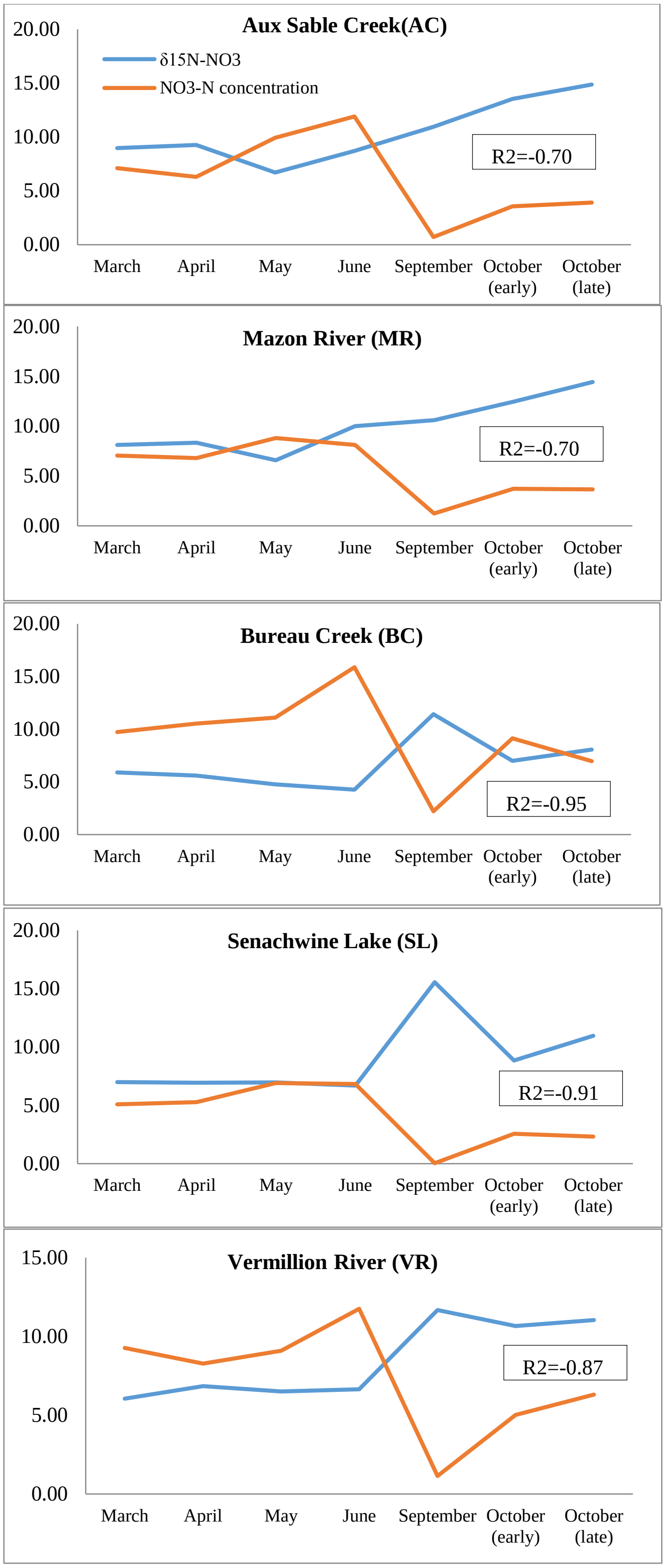


Figure 15 Correlation between nitrate concentration and $\delta^{15}N\text{-}NO_3$ of samples from

agricultural tributaries in 2008. The changes in $\delta^{15}N-NO_3$ values are highly correlated with changes in nitrate concentration, with R^2 values ranging from -0.70 to -0.95.

TABLES

Table 1 Nitrate yield (kg N/ km^2• month) variation in major tributaries in the UIRB and two Illinois River stations (italics) between spring (April) and fall (September), 2008. Nitrate flux calculation was based on measured nitrate concentration, gauged tributary discharge, and area of tributary watershed. The calculation of fall to spring ratio demonstrates that urban watersheds (e.g., Du Page River) have more constant nitrate export in both spring and fall, while agricultural watersheds (Kankakee River, Aux Sable Creek, Mazon River, Vermillion River, and Bureau Creek) have fall nitrate yield much lower than the spring yield. Watersheds with mixed land use (e.g., Fox River) are also less influenced seasonally.

Tributary	**Nitrate yield (NO_3-N kg/ km^2• mon)**		**Fall to Spring ratio**
	April (Spring)	**September (Fall)**	
Du Page River	139.00	123.55	0.89
Kankakee River	79.28	10.88	0.14
Aux Sable Creek	81.46	5.24	0.06
Mazon River	76.98	5.50	0.07
IL River at Marseilles	*114.78*	*81.95*	*0.71*
Fox River	120.84	37.50	0.31
Vermilion River	139.20	4.80	0.03
Bureau Creek	306.36	12.25	0.04
IL River at Henry	*163.74*	*85.47*	*0.52*

CHAPTER 3

3. MODELING OF NITRATE SOURCES, TRANSPORT, AND DENITRIFICATION IN THE UPPER ILLINOIS RIVER BASIN: AN APPLICATION OF SWAT

Chapter 3 will be published in future as follows with modifications:

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3.1. Introduction

The dead zone at the northern Gulf of Mexico (NGOM) is fueled by anthropogenic nutrient loadings from the Mississippi River Basin (MRB), and has generated great concern because of its threats to commercial and recreational gulf fisheries (USEPA, 2011). In 2007, the measured size of the hypoxic zone was 20,500 square kilometers. The EPA Gulf Hypoxia Action Plan provides nutrient reduction strategies targeting at least a 45% reduction in riverine total nitrogen and phosphorus load, which is extremely challenging under the current situation (USEPA, 2008).

To help control the annual nitrate flux to the NGOM and preserve water quality, it is critical to understand the distribution and behavior of nitrate within the Illinois River Basin. Flowing through one of the most productive farming regions and populated metropolitan areas in the central US, the Illinois River contributes a considerable proportion (16-19%) of the total annual nitrogen (N) flux from the MRB (Goolsby, 1999). The average annual nitrate flux from the Illinois River was estimated to be 113,660 metric tons per year (Goolsby, 1999). The concentration of riverine nitrate in the Illinois River has increased by more than two fold in the last century (Goolsby, 1999). Variations in annual inputs of water and nitrogen make it difficult to identify the relative importance of different human activities and hydrological conditions to nitrate export. Modeling is thus a suitable approach to examine how land use impacts the delivery of nutrient and the effectiveness of management actions at various scales. There are huge potentials in modeling studies that will allow us to enhance knowledge of nitrate sources and sinks in order to achieve the nitrogen reduction goal.

The Soil and Water Assessment Tool (SWAT) has demonstrated its powerful applications in simulation of soil, water, sediment, and nutrient processes. It has been applied worldwide to investigate various topics related to land management and water resources, such as crop yield and nitrate leaching in agricultural regions (Akhavan et al., 2010), groundwater recharge and baseflow (Arnold and Allen, 1999), and hydrologic response to climatic variability (Wu, 2007). Extensive work has also been carried out using SWAT simulations to study watershed nutrient export (Hu, 2007; Lam, 2010), and predict impact of alternative management practices on water quality and basin responses (Ullrich, 2009; Santhi et al., 2001; Jiang, 2014; Yan et al., 2013). However, there are large uncertainties within model outputs, usually induced by input data errors, model structure uncertainties, and uncertainties in the observations that are used for model calibration (Griensven, 2005). It is critical to evaluate model accuracy when the model results could affect management practices.

We selected SWAT to simulate both water discharge and nitrate load from various point and non-point sources in the Upper Illinois River Basin (UIRB). The objectives of this study are the following: 1. simulating nitrogen export from the UIRB; 2. evaluating the calibrated model prediction on nitrate export within the watershed using observed data; 3. examining if SWAT is capable to estimate denitrification processes; 4. improving simulation by incorporating denitrification into SWAT; 5. Apply model output to study hydrological and land use management effects on nitrate processes. Towards these goals, we hope this study will provide an improved scientific basis for better management actions to reduce nitrate load from point and nonpoint sources.

3.2. Materials and Methods

3.2.1. Description of the study area

The UIRB drains the total area of 37,353 km^2, from its headwaters at Lake Michigan to the Peoria Lock on the Illinois River at Peoria, IL. It covers 38 counties in 4 states: 26 counties in northeastern Illinois (>50% of the basin area), 13 counties in northwestern Indiana, 5 counties in southeastern Wisconsin, and 1 county in southeastern Michigan (<0.1% of the basin). Figure 16 shows the location of the UIRB and its major tributaries.

Agriculture accounts for about 75% of the land use in the entire UIRB, and urban areas account for about 17% of land use (Figure 17). For the agricultural area, increasing demands for corn and soybeans have caused intensified cultivation of these crops, which are the two principal row crops in the UIRB. About 36.9% of the total UIRB area is planted with corn, and 21.6% with soybean, according to the cropland data of 2008 from the National Agricultural Statistics Service. Point sources in the Chicago area continue to be another major source of nutrients and other contaminants in the UIRB. There are about 196 wastewater reclamation plants (WRP) discharging wastewater to streams in the basin, and most of them locate in the greater Chicago area (Arnold and Ruhl, 1999). The inland area (colored in maroon) in Figure 17 overlaps the greater Chicago area. The dominant land use of the inland area is urbanized land. Most of the WRPs of the UIRB locate in this area, including the five biggest WRPs of the MWRDGC (Metropolitan Water Reclamation District of Greater Chicago), namely Stickney, Calumet, Northside (O'Brien), Kirie, and Egan, in the order of decreasing capacity. These plants range in capacity from 4.5 million m^3 per day at the Stickney plant, which is the world's largest WRP, to 0.09 million m^3 per day at the Egan plant. The boundaries of the MWRDGC cover more than five million residents and thousands of industries of Cook County, Illinois. About 5.3 million m^3 of wastewater is generated each day within this district.

The climate of the UIRB is humid continental, characterized by cool, dry winters and warm, humid summers. The average annual temperature (1961-1990) ranges from 7 ℃ to 11 ℃ and the average annual precipitation (1961-1990), including liquid equivalent of snowfall, ranges from less than 81 cm to more than 96 cm. The elevation ranges from 135 m to 380 m above sea level. The entire UIRB is underlain by Precambrian granitic rocks at depths ranging from 300 m to 2,133 m below the surface, which are overlain by Cambrian sedimentary rocks, predominantly sandstone. The thickness of Cambrian formations ranges from 300 m to 1,500 m, with thinner formation mostly lying in the northern part of the basin and thicker formations in the southeastern part. Overlying the Cambrian rocks are Ordovician rocks composed mainly of limestone and dolomite, and minor portions of sandstone and shale, with thickness ranging from 300 m (in the northern and western) to 457 m (in the southeastern) (USGS, 1999). Five major Quaternary glacial periods shaped the land-surface features in the UIRB, resulting in the unconsolidated glacial deposits and glacial features (e.g., outwash plains, moraines, kettle lakes, drumlins) that cover most of the study area.

3.2.2. Database development for the model

SWAT is a physically based continuous time model that operates on a daily time step. It was developed by Dr. Jeff Arnold in the early 1990. It incorporates features of several valuable USDA-ARS (Agricultural Research Service) models, which were designed in response to the Clean Water Act, and is a direct outgrowth of SWARRB (Simulator for

Water Resources in Rural Basins), a continuous time step model that was developed to simulate nonpoint source loadings from watersheds (Neitsch et al., 2011). Constant updates and improvements by the development team as well as the research community have made SWAT a powerful tool for simulation and prediction on various scales.

The SWAT model construction and calibration require a large amount of data input and empirical parameters. Main input include the following: topography, stream network, land use, soil properties, agricultural operations (e.g., plant, fertilizer application, harvest, irrigation, tillage, and tile drainage), climate, reservoirs and ponds, point source pollution and its location. Most of the data are available from public websites in the United States, or can be generated using Geographic Information System (GIS). Detailed input data sources for model simulation in this study are listed in Table 2.

The UIRB SWAT model was constructed to simulate the period from 1990 to 2009.

3.2.3. Watershed delineation

The 30-m DEM and the USEPA's Reach File 1 (RF1) were used for the delineation of subbasins and stream networks. The stream networks were pre-processed so that there was only one stream per subbasin. There were 142 subbasins generated during watershed delineation. However, given the significant amount of WRP effluent from the Greater Chicago Area, an inlet to represent the combined point source input was added to the basin where the Chicago Sanitary and Ship Canal joins the Des Plaines River. Subbasins upstream of this inlet were thus considered to be inland as shown on Figure 17. The final number of subbasins was reduced to 132, by excluding an inland area (overlap with the

Greater Chicago Area) from the UIRB and adding the inland to the basin as an inlet of point source.

In SWAT, grid cells are generated in each subbasin based on land use, soil type, and slope. Cells that share the same soil type, land use and slope within each subbasin are grouped together and converted into polygons that represent HRUs (Hydrologic Response Units). There are 4880 HRUs generated in this study. The land use map for UIRB was generated based on USGS 2001 National Land Cover Data for non-agricultural land classifications and the 2008 CDL (Cropland Data Layer) for agricultural land classifications. The soil map was obtained from the National Resources Conservation Service (NRCS) State Soil Geographic (STATSGO) database, which was already implemented as part of SWAT model. The land surface slope of UIRB was divided into three categories during HRU definition: <1%, 1-5%, and >5%.

3.2.4. Point sources

Considering the large discharge and associated contribution of nitrate from the treated wastewater of the inland area (Figure 17), combined effluents from main wastewater treatment plants were added to the model as an inlet. Selection of the plants was based on the size of the plant, discharge amount and distance from the watershed mainstream. The largest five plants were included in this model: Calumet, Egan, North Side, Kirie, and Stickney.

3.2.5. Weather

SWAT requires daily precipitation, minimum and maximum temperature, relative humidity, solar radiation, and wind speed to simulate daily or sub-daily watershed responses (Demissie et al., 2012). Daily rainfall and temperature measurements from 1990 to 2009 were downloaded from NOAA's National Climatic Data Center (NCDC) weather stations in and around the UIRB. There was one weather station assigned to each subbasin. The observed data were interpolated to the centroids of the 132 subbasins by using the inverse distance weighting interpolation method over five nearest neighbor weather stations, as described in Demissie and Yan (2012) and Shepard (1968).

3.2.6. Fertilizer

Fertilizer application is an important source of nitrate export from the basin, thus fertilizer usage for corn and soybean crops was manually added to the model input of agricultural management. The distribution of fertilizer is not consistent within the basin, or even within one subbasin. Fertilizer application rate ((kg/ha • yr) is defined as the amount of fertilizer (kg) applied on one hectare of area annually. The rate of one subbasin was assumed to be the same as that of the county where the subbasin located, while county-level rate was calculated based on state-level fertilizer usage and the assumption that county-level fertilizer use is directly proportional to its crop yield (Demissie et al., 2012), as in the equation below:

$$F\ (crop_i, county_j) = F(crop_i, state_k)\frac{Y(crop_i, county_j)}{Y(crop_i, state_k)} \qquad (1)$$

Where, $\mathrm{Y(crop_i, county_j)}$ and $\mathrm{Y(crop_i, state_k)}$ are yields of crop type *i* from county *j* and state *k*, respectively; $F\ (\mathrm{crop_i, county_j})$ and $F(crop_i, state_k)$ are fertilizer application rates over crop *i* in county *j* and state *k* respectively. In this study, crop types are corn and soybeans. However, some subbasins may not be completely inside one county. For those lying across two or more counties, a weighted average based on intersecting area between county and subbasin was used to estimate subbasin fertilizer use. Data sources for fertilizer application are shown in Table 2.

3.2.7. Tile drains

Tile drains were added at the beginning of the simulation. In Illinois, predominant soils have poor internal drainage, thus a big portion of the farm lands are underlain by tiles to remove excess water (Keeney and Muller, 2000). The layers of land use, soil type, and slope of HRU were used to decide tile drainage locations. We applied the same settings for tile drains as those used by Demissie and Yan (2012) in their SWAT modeling study of the Upper Mississippi River Basin: the depth to the tile drain was set as 850mm; the time to drain soil to field capacity was 48 hours, and the drain tile lag time was 12 hours. Crops grown on poorly drained soils (hydrologic groups C and D) on a surface with <1% slope were assumed to have subsurface tile drains.

3.2.8. In-stream denitrification

Denitrification is an important process for nutrient transport and transform. It is important to quantify rates and controls of in-stream denitrification in order to better understand and predict effects of land use management on water quality and nutrient export. Many studies have concluded that the removal of nitrate via denitrification is responsible for reduction in nitrate flux, and is highly efficient during months when nitrate concentration and discharge are low, mostly during late summer to fall (Alexander et al., 2008; Böhlke et al., 2009; David et al., 1997; Panno et al., 2008).

In SWAT, nitrate removal from the watershed is via plant uptake, transport with surface runoff, lateral flow or percolation, and denitrification in soil layers, which is a function of soil water content, temperature, and presence of a carbon source and nitrate. SWAT also applies an exponential decay weighting function to account for nitrate lost in the shallow aquifer due to chemical and biological processes (Neitsch et al., 2011). However, nitrate removal in the stream is only simulated as the result of algal uptake. In-stream denitrification has not been considered by previous modeling efforts. Here, we present a significant improvement in the model ability to simulate nitrate process by implementing the following denitrification equation into SWAT codes (Alexander et al., 2009):

$$NO_{3_{i,out}} = NO_{3_{i-1,out}} e^{-k_i t_i} + NO_{3_{i,lat}} e^{-0.5 k_i t_i} \qquad (2)$$

where, $NO_{3_{i-1,out}}$ is nitrate flux (NO3_OUT from SWAT output file) from the upstream reach i-1, $NO_{3_{i,lat}}$ is the lateral nitrate flux from the current subbasin i (surface runoff, lateral flow, groundwater flow), t_i is the residence time, and k_i is the volumetric-related, first order reaction rate constant (units of time^{-1}). The lateral nitrate flux has approximately residence time $0.5t_i$ (Alexander et al., 2009). The reaction rate constant k_i can be calculated as follows:

$$k_m = b_0 C_m^{b1} H_m^{b2} [\sin(2\pi T_m)]^{b3} [\cos(2\pi T_m)]^{b4} \varepsilon_m \qquad (3)$$

which is simplified into the following equation during SWAT implementation:

$$k_m = b_0 C_m^{b1} H_m^{b2} \qquad (4)$$

where, k_m is the rate constant, b_1 and b_2 are estimated dimensionless coefficients, b_0 is an estimated model intercept with units of the reaction rate constant, C_m and H_m are respectively water-column nitrate concentration and reach depth. Reach depth can be calculated based on SWAT output of reach discharge and reach geometry. Böhlke et al. (2009) summarized the values for the coefficients, which were applied in this study: b_0 = -0.785, b_1=-0.524, b_2=-1.097.

This in-stream nitrate transport equation is based on a one-dimensional version of the advection-dispersion equation that includes non-conservative transport and assumes negligible effects from solute mixing related to dispersion and transient storage (Alexander et al., 2009).

3.3. Model calibration and validation

Model calibration and validation are required before applying the model for future studies. During calibration, important variables such as runoff curve number that are not well defined physically for the specific study area can be adjusted for a better simulation-observation fit. The calibration is conducted as follows: 1. Identify key parameters via sensitivity analysis and referencing previous studies; 2. Calibrate model by adjusting selected sensitive parameters; 3. Validate model by evaluating model simulations that are not used during calibration.

3.3.1. Sensitivity analysis

Sensitivity analysis is important to screen the most influential parameters from a great number of variations that are possibly intrinsically correlated. It limits the number of parameters for optimization and saves simulation time. Observed river discharge data and nitrate load data were included during sensitivity analysis to identify parameters that were affected by the characteristics of the study basin and to which the model was the most sensitive (van Liew and Veith, 2010).

The sensitivity analysis for flow calibration was performed using the PARASOL (PARAmeter SOLution) algorithm as implemented in SWAT model, which is based on the LH-OAT (Latin Hypercube One-factor-at-A-Time) method. For nitrate calibration, sensitivity analysis was performed using the SUFI-2 (Sequential Uncertainty Fitting) procedure implemented in the SWAT Calibration and Uncertainty Programs (SWAT-CUP) developed by Abbaspour (2008). This method allows the user to specify rational ranges of parameters (Demissie et al., 2012). The selected parameters for flow and nitrate calibrations, and results of sensitivity analysis are listed in Table 3.

According to the sensitivity analysis results (Table 3), parameters that affect flow calibration the most (ranking No.1 to No.3) are the ones that control surface runoff, groundwater transport, and plant uptake. Parameters that have the greatest impact on nitrate calibration are the ones that control denitrification reaction extent, and plant N uptake.

3.3.2. Calibration and validation

In this study, flow and nitrate calibrations were carried out separately with different simulation periods and sensitive parameters (Table 3). Flow calibration was conducted first because discharge could have great impact on nitrate export (van Griensven, 2006). Measurement uncertainty is also assumed to be less with hydrologic data (stream discharge) since estimated flow was developed from daily gauge readings (White and Chaubey, 2005).

The goal for calibration is to optimize the selected objective functions. The model is calibrated monthly using the Nash-Sutcliffe coefficient, R_{NS}^2, which is an indicator of the model's ability to predict based on the goodness-of-fit between observed and simulated data. R_{NS}^2 is defined as:

$$R_{NS^2} = 1 - \frac{\sum_{i=1}^{n}(O_i - P_i)^2}{\sum_{i=1}^{n}(O_i - O_{avg})^2} \qquad (5)$$

where, O is measured value, P is predicted output and i equals the number of values (Nash and Sutcliffe, 1970). A perfect fit is achieved when R_{NS}^2 equals 1. Since R_{NS}^2 is sensitive to outliers (Kirsch et al., 2002), the monthly coefficient of determination (R^2) is also calculated as:

$$R^2 = \left[\frac{\sum_{i=1}^{n}(O_{i-}O_{avg})(P_{i-}P_{avg})}{\left[\sum_{i=1}^{n}(O_{i-}O_{avg})^2 \sum_{i=1}^{n}(P_{i-}P_{avg})^2\right]^{0.5}}\right]^2 \qquad (6)$$

3.3.3. Flow calibration and validation results

The hydrologic process in SWAT is based on the following water balance shown in equation 7:

$$SW_t = SW_0 + \sum_{i=1}^{t}(R_{day} - Q_{sur} - E_a - W_{seep} - Q_{gw})_i \qquad (7)$$

where, t is the time step index (days), SW_t is the final soil water content (mm water) by the end of time step t, SW_0 is the initial soil water content, $R_{day}$is the amount of precipitation (mm) on day i, $Q_{sur}$is the surface runoff (mm) on day i, $E_a$represents evaporation (mm), W_{seep}represents the amount of water entering the vadose zone from the soil profile on day i (mm), and $Q_{gw}$is the amount of return flow (mm) on day I (Neitsch et al., 2011).

Flow calibration was conducted for the simulation period of 1996-2008, and validation was performed for 1993-1995. Parameter adjustments made can be seen in Table 3. The computational results of discharge at the basin outlet and the town of Marseilles (Figure 17) were calibrated with measured data from three USGS gauges: No.1: USGS site #5543500 (Illinois River at Marseilles), No.2: USGS site #5568000 (Mackinaw River near Green Valley), and No.3: USGS site #5568500 (Illinois River at Kingston Mines). Gauge No.1 was selected because of the availability and integrity of the data through the entire modeling duration. However, since the USGS does not have a monitoring station at the outlet of the study basin, the discharge at the basin outlet was calculated as the difference between gauge No.2 and No.3, applying drainage area as a scale factor.

The results of flow calibration are shown in Figure 18a and 18b, with R^2 value of 0.82 and R_{NS}^2 value of 0.67 at the basin outlet, and R^2 value of 0.83 and R_{NS}^2 value of 0.57 at the near-mid-point Marseilles. The values of R^2 tend to be higher than that of R_{NS}^2, because an outlying value on a single event (such as a flood event) can significantly lower the R_{NS}^2 while R^2 is only slightly affected. The flow calibration was performed for the period from 1996 to 2008, because the first three years (1990-1992) were used as model warm-up period, and the following three years (1993-1995) were used for flow validation.

Flow validation was performed at both basin outlet and Marseilles for the simulation period of 1993-1995 (Figure 18c and 18d). R^2 values are 0.83 and 0.82, respectively at basin outlet and Marseilles, and R_{NS}^2 values are 0.53 and 0.42 respectively. R^2 and R_{NS}^2 values indicate the good agreement between simulated and observed values, and so calibration was considered successful. The application of observed precipitation data significantly enhances model efficiency in hydrologic simulation. Model was able to predict extreme events (low flow, and flood), as is evident from the cumulative distribution of the flow (Figure 19). However, model simulated discharge and base flow is generally lower than observed flow.

3.3.4. Nitrate calibration and validation results

Nitrate calibration was conducted for the simulation period of 2003-2009, and validation for 1999-2002, at the basin outlet and Marseilles (Figure 17). Parameter adjustments can also be seen in Table 3. Only monthly measurements of stream nitrate were available due to limited resources, but applying these data as monthly averages could induce huge bias, especially when measurements were taken under special circumstances, such as extreme weather conditions. It is important for SWAT calibration that nitrate concentration and loads are accurately estimated for times when no data were available. LOAD ESTimator (LOADEST) was thus applied to generate monthly nitrate output data, which were then compared with SWAT simulations during nitrate calibration.

LOADEST is a FORTRAN program developed to estimate constituent loads in streams and rivers, based on statistical estimation methods (Runkel et al., 2004). Given a time series of streamflow, constituent concentration, and additional data variables (various functions of streamflow, decimal time, and additional user-specified data variables), LOADEST can assist users in developing regression models that are used in the estimation of constituent load over a user-specified time interval. LOADEST has been widely used in the estimation of nitrogen and phosphorus loads in many riverine nutrient studies (Goolsby et al., 2000, 2001; Hooper et al., 2001; Aulenbach and Hooper, 2006; Maret et al., 2008). The USGS SPARROW (SPAtially Referenced Regressions On

Watershed attributes) model also applied LOADEST estimation as “observed” loads in its calculation (USGS, 2009).

Observed discharge data from USGS gauges and measured nitrate concentration were used to extrapolate monthly nitrate load from 1999 to 2009, using the AMLE (Adjusted Maximum Likelihood Estimation) regression and the 9th model in LOADEST. The Nash-Sutcliffe coefficients of LOADEST load estimation of nitrate at two locations (Peoria and Marseille) are respectively 0.76 and 0.87, and the R^2 values are respectively 0.95 and 0.90. These R^2 and R_{NS}^2 values for nitrate load estimation are considered very good, and thus are suitable to be used as “observed” data in SWAT calibration.

The results of nitrate calibration and validation are shown in Figure 20. The R^2 value and R_{NS}^2 value for calibration are respectively 0.60 and 0.57 at the basin outlet, and are 0.55 and 0.37 at the Marseilles. For validation, the R^2 value and R_{NS}^2 value are respectively 0.51 and 0.46 at the basin outlet, and are 0.55 and 0.40 at the Marseilles. The statistics fall between the categories of good and satisfactory results (Moriasi et al., 2007), and calibration is considered successful. Model was able to predict extremes as shown in the cumulative distributions (Figure 21). There is good agreement between SWAT simulation and LOADEST output of nitrate, although SWAT tends to underestimate high nitrate output at the basin outlet.

3.4. Results and Discussion

3.4.1. Denitrification

Our simulation provides access to quantifying in-stream nitrate removal over watershed scale. Simulation results were compared with the output of the SWAT version that had no in-stream denitrification implementation. SWAT produces NO_3^- output of reaches

(NO3_OUT) at the end of each simulation. The NO3_OUT at reach *i* is the total load associated with a stream reach that arrives at the downstream end of the selected reach *i*, in unit of mass (kg N) over selected time (month, year, day). It is not the incremental delivered load of reach *i* only, but rather the sum of loads delivered by all upstream reaches *i-1, i-2, i-3…*

The in-stream denitrification amount is calculated as the difference in NO3_OUT results between two SWAT versions as in the following equation:

$$Denitrification_i = NO3\_OUT_{i,no-deni} - NO3\_OUT_{i,deni} \qquad (8)$$

where, $Denitrification_i$ is the mass of nitrate removed within river section *i*, $NO3\_OUT_{i,no-deni}$ is NO_3^- load at reach *i* simulated by initial SWAT2009 version without stream denitrification implemented, and $NO3\_OUT_{i,deni}$ is NO_3^- load at reach *i* simulated by SWAT with in-stream denitrification implementation. Since the first three years in our SWAT simulations is the model warm-up period, monthly outputs from 1993 to 2009 of 16 subbasins located along the main stem of the Illinois River were selected to calculate temporal and spatial variations in stream denitrification within the UIRB. Results are plotted in Figure 22.

Among the 16 main stream subbasins, #24 is the most upstream subbasin and closest to the great Chicago area and #131 is at the outlet of UIRB, thus the most downstream subbasin. Figure 22 exhibits cumulative amount of denitrification along the waterway. The amount of denitrification increased substantially downstream, which reveals aggregate denitrification effects along the Illinois River Waterway. This trend was observed in all 17 simulated years (Figure 22a), and represents a consistent pattern of nitrate removal processes along the waterway. However, the calculated denitrification does not represent the fraction of nitrate removed within each reach.

A seasonal pattern at the basin scale was also observed in Figure 22b. The maximum in-stream denitrification (red) occurred during late summer to fall, from June to September, and the least denitrification (blue) occurred during winter to spring, mostly from December to February. The temporal changes were mostly in response to changing weather and stream flow. Böhlke et al. (2009) studied the denitrification process within a small agricultural watershed in Illinois, and concluded that denitrification could exhibit seasonal variations, with relatively high values in summer and fall. A relative dry period (late summer to fall) with low stream water depth and velocity provides the optimum condition for denitrification. Since in-stream denitrification occurred mainly in benthic sediments (eg: Böhlke et al., 2009; Alexander et al., 2009), the denitrification efficiency is enhanced by slower stream velocity and shallower water depth, which results in greater interaction of riverine nitrate with denitrifying bacteria in stream sediment. Temperature effects could also cause seasonal variations of stream denitrification, by changing microbial community structure and enzymatic processes, which are complex functions of temperature and dissolved oxygen content (Böhlke et al., 2009).

3.4.2. Hydrological effects on nitrate transport

SWAT model output of discharge, precipitation, and nutrient load allowed estimation of the effect of hydrological components on denitrification and nitrate removal in the river networks on watershed scale.

Figure 23 contains a series of model simulated nitrate output and observed precipitation plots on subbasin level. Annual precipitation (mm) and NO_3^- load (kg N) of 132 model subbasins were plotted for comparison over the period of 2000-2009, the most recent ten years in the model simulation. A strong positive correlation between the amounts of precipitation and NO_3^- export on basin level can be observed in Figure 23. For example, as one of the driest year in terms of precipitation, year 2005 had an average annual precipitation amount of 723 mm in UIRB, compared to 1160 mm in 2009 and 1190 in 2008, the two most humid years. The total basin NO_3^- load (sum of 132 subbasin export) of 2005 was estimated to be less than 50% of that of 2009 and 2008, respectively. Similarly, 2003 and 2004, two relatively dry years, had total NO_3^- outputs observably lower than other years.

On the subbasin level, significant influence of precipitation on NO_3^- export can also be observed (Figure 23). The variation in precipitation amount is reflected in the spatial variation of subbasin NO_3^- loads. Areas with relatively intense rainfalls have higher nitrate output. A given area could behave differently in years having different meteorological conditions. For example, the Fox River Basin—at the northern tip of the UIRB on Figure 23—had low nitrate export in 2002 and 2003 (<2500 tons N) because the basin experienced dry periods in these two years. The nitrate export of the Fox River Basin increased substantially in 2008 (8843 tons N) and 2009 (7615 tons N), when this area received more precipitation.

Precipitation is the driving factor that controls stream discharge, water depth, and velocity, which have profound effects on nitrate transport processes. Royer and David (2006) conducted a 12-year intensive monitoring program to study the timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois. They found that discharges greater than median value were responsible for nearly all nutrient export in the basin, and these mostly occurred in a period from mid-January to June, while extreme discharges (≥ 90th percentile) played an important role in nitrate export. Their simulations showed that a 50% reduction in nutrient loads during period of low discharge (< median) would only reduce total export by 2%. Chang and Kendall (2002) and David et al. (1997) both reached the conclusion that nitrate concentration and flux in river and discharge were positively correlated under the influence of weather among agricultural sites and exhibited seasonal patterns.

However, many other anthropogenic factors also control nitrate output, such as land use type, fertilizer application rate, amount of manure and fertilizer application, and urban wastewater discharge. Subbasins with the highest nitrate export are mostly in the Kankakee River Basin, Iroquois River Basin, and Mazon River Basin, which are dominant by agricultural land use, with extensive fertilizer usage and discharge via tile drainage.

3.4.3. Model application: land use scenarios

The effect of fertilizer application rate on nitrogen export is of special interest to this study. The agricultural input of nitrogen fertilizer enters the waterway via tile drainage or leaching from soil. By altering fertilizer application rate in the model input, we are able to simulate the changes in basin nitrate output under various management plans, and make a better strategy.

The "20-in-10" goal established by the Bush Administration in 2007 calls for a goal of reducing gasoline usage by 20% in the next 10 years, which is to be achieved by "increasing the supply of renewable and alternative fuels by setting a mandatory fuels standard to require 36 billion gallons of renewable and alternative fuels in 2017"

("Twenty In Ten: Strengthening America's Energy Security"). The U.S Energy Independence and Security Act (2007) mandates the production of 136 billion liters of biofuel by 2022; it also estimates that the production should reach 77.6 billion liters in 2015. This goal requires a 75% increase of biofuel production based on current (2015) level, and will dramatically affect land use pattern and fertilizer application, and alter the N budgets as a result of intensified agricultural activities, especially in the Midwest.

Quantifying the impact of fertilizer application on basin nitrate export is important for policy makers and farms to establish better management plans, and to achieve good balance between corn production and environmental preservation. Figure 24 shows simulated changes in UIRB basin nitrate export (kg N) resulting from changes in the fertilizer application rate (kg/ha • yr), applying SWAT2009 version with stream denitrification implemented. Reducing the fertilizer application rate by 10%, 25%, and 50% can result in respectively 6%, 16%, and 31% reduction in nitrate export on the basin level at the end of the simulation (2009). Increasing the current SWAT fertilizer application rate by 10%, 25%, and 50% can cause an increase in basin nitrate export ranging from 3-10%, 8-25%, and 16-51% respectively during the entire simulation period. At the subbasin level, about 37% of the 132 subbasins have changes in nitrate export greater than 15% after changing fertilizer application rate by ±25%, but over 36% subbasins have changes smaller than 10%, and over 22% subbasins have changes smaller than 5%. Also, approximately 34% subbasins have 30% changes in nitrate export associated with ±50% changes in fertilizer application rate, over 22% subbasins have changes in nitrate export less than 10%, and 13-20% subbasins have changes smaller than 5%.

To enhance corn yields per unit area and maximize profitability, farmers often increase fertilizer applications (Demissie et al., 2012). The calibrated UIRB model was also applied to evaluate the potential influence of increasing fertilizer application rate over current corn production and yield at basin and subbasin levels. The simulation demonstrates that a 25% increase in fertilizer application rate is required in order to achieve a 15% increase in corn production (kg) at the basin level, and 50% increase in fertilizer application rate for 30% increase in corn production. At the subbasin level, after increasing fertilizer application rate by 25%, approximately 3% of the 132 subbasins have less than 10% increase in corn yield (kg/ha), and 30% subbasins in total have less than 15% increase in corn yield. Similarly, after increasing fertilizer application rate by 50%, only 50% of the subbasins show more than 30% increase in corn yield.

Our data suggest that to achieve the biofuel production goal will require more actions than simply raising fertilizer application amount, which does not result in a proportional increase in corn production, however can lead to significant enhancement in basin nitrogen loading and deterioration of water quality. Crop nitrogen uptake efficiency is a limiting factor that needs to be considered when people are trying to improve corn production. The surplus N input to the soil that cannot be assimilated by plants can enter the environment via leaching in the soil and be transported in the stream network, and cause severe environmental consequences. Response to increased N input varies among subbasins. Some subbasins are more sensitive to changes in fertilizer input compared to others, which is presumably a result of integrated effects of land use, topography, weather condition, and crop planting area, thus specific management plans need to be made targeting at different subbasins in order to maximize the benefit.

3.5. Conclusions

The denitrification implementation in SWAT improved the effectiveness for model simulation of nitrate loads. By adding denitrification, we were able to study the in-stream nitrate removal process that had not been simulated in SWAT before, thus we were able to achieve a better understanding of the basin nitrogen budget from the modeling. The implementation provided a visualization of quantification of denitrification and nitrate export on a basin level. A seasonal variation in stream denitrification rate is observed from model simulated results: higher denitrification during late summer and fall, and low denitrification during winter. The model simulation also demonstrated enhanced denitrification amount downstream on the main Illinois River.

The SWAT output was also used to estimate the effect of hydrological components on denitrification and nitrate removal in the river networks on watershed scale. Precipitation, as a driving force that controls stream hydrology, has great impact on the simulated nitrate loads. A strong positive correlation between the amounts of precipitation and NO_3^- export on basin level can be observed from model output.

Our study also showed that increasing fertilizer application does not always lead to rapid increase in corn production, however, it can significantly enhance nutrient export. Extra caution should be used when trying to achieve the biofuel production goal. SWAT modeling has strong applications to future policy making. There are huge potentials in modeling studies that will allow us to enhance our knowledge on management of N sources and sinks. Models can be further combined with future climate and population scenarios to study how changes in anthropogenic inputs affect nutrient export, and thus the Gulf environment. One example that can be combined with SWAT prediction is the

EPA FML (Future Midwest Landscapes) project scenarios, which is a decision tool kit that can be used to study biofuels and ecosystem services in the Midwestern U.S. by developing and analyzing alternative future scenarios and collaborating across organizations. Modeling is a suitable approach to examine the effectiveness of changes in management and policy and how they will impact the delivery of N to the coast at the watershed or national scale.

FIGURES

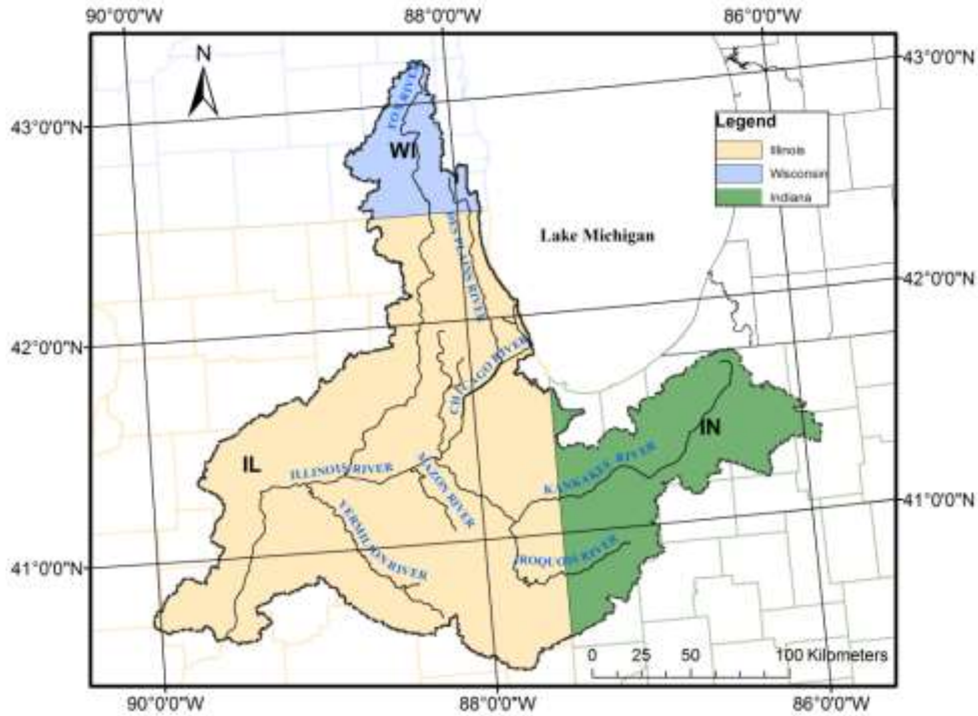


Figure 16 The location of the Upper Illinois River Basin and its major tributaries.

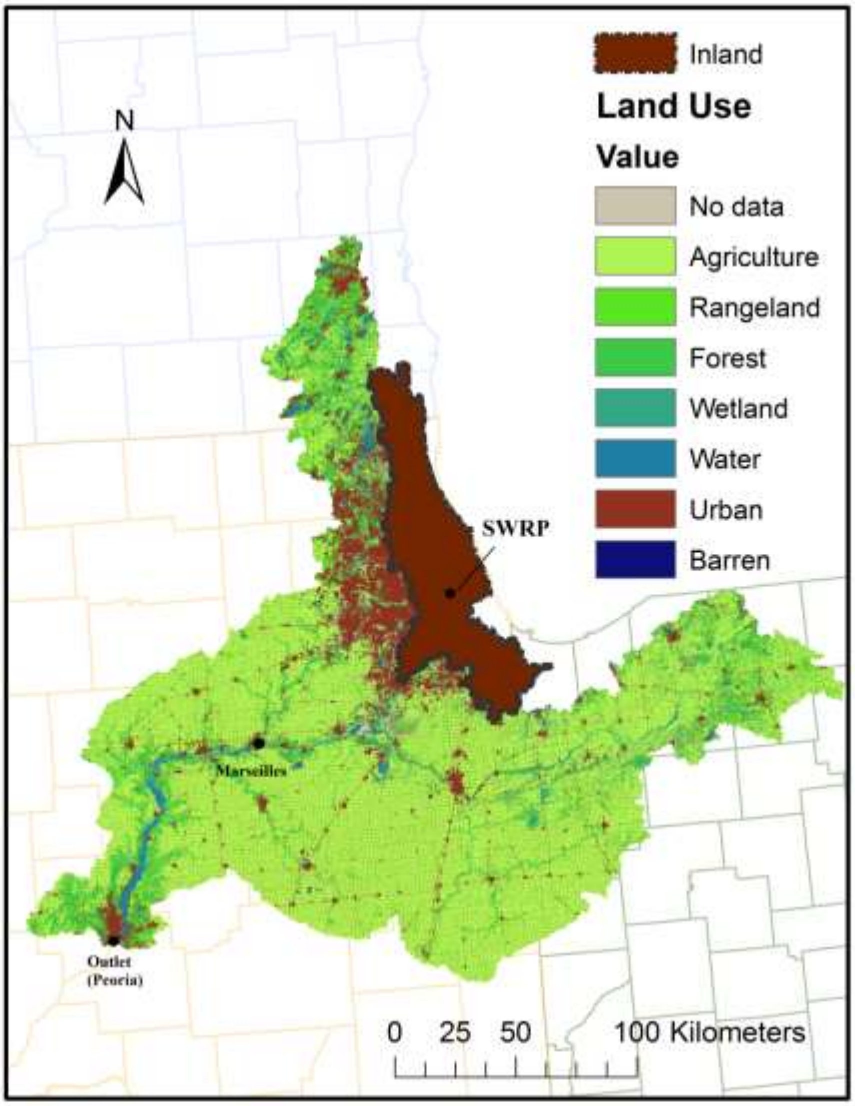
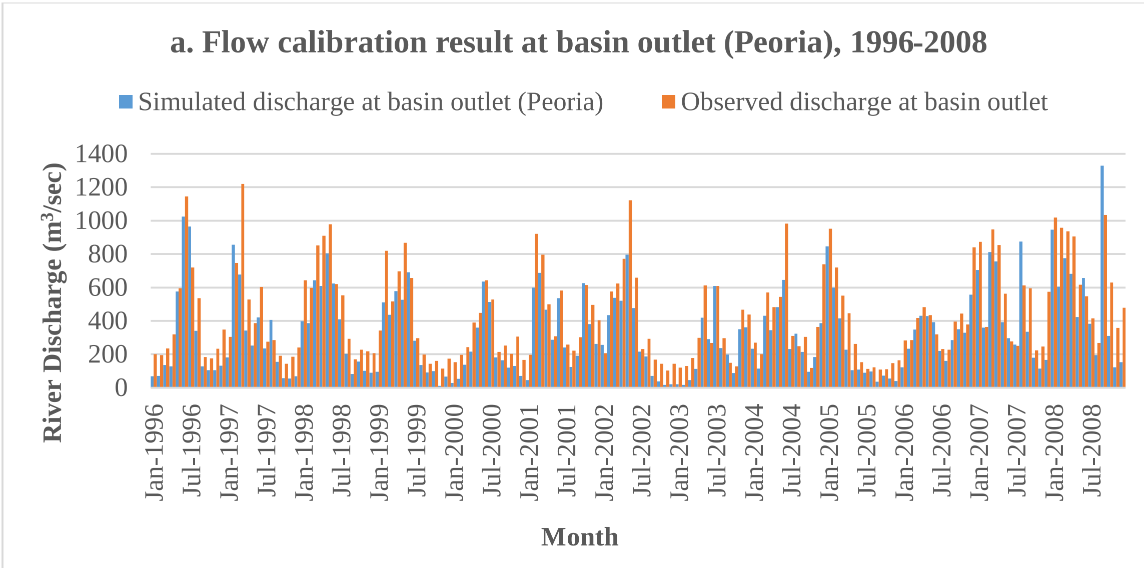
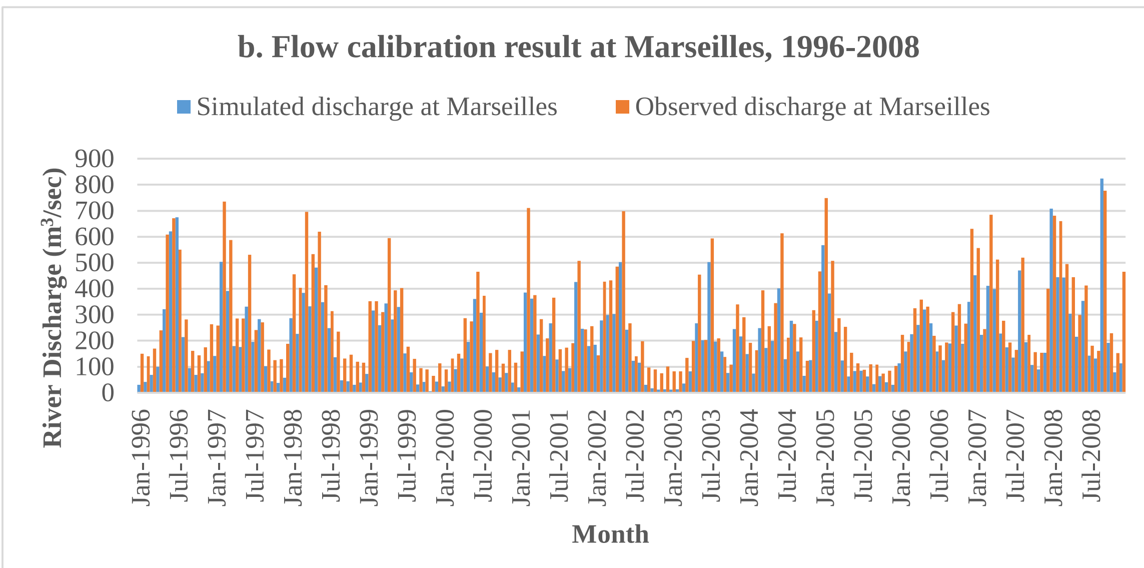
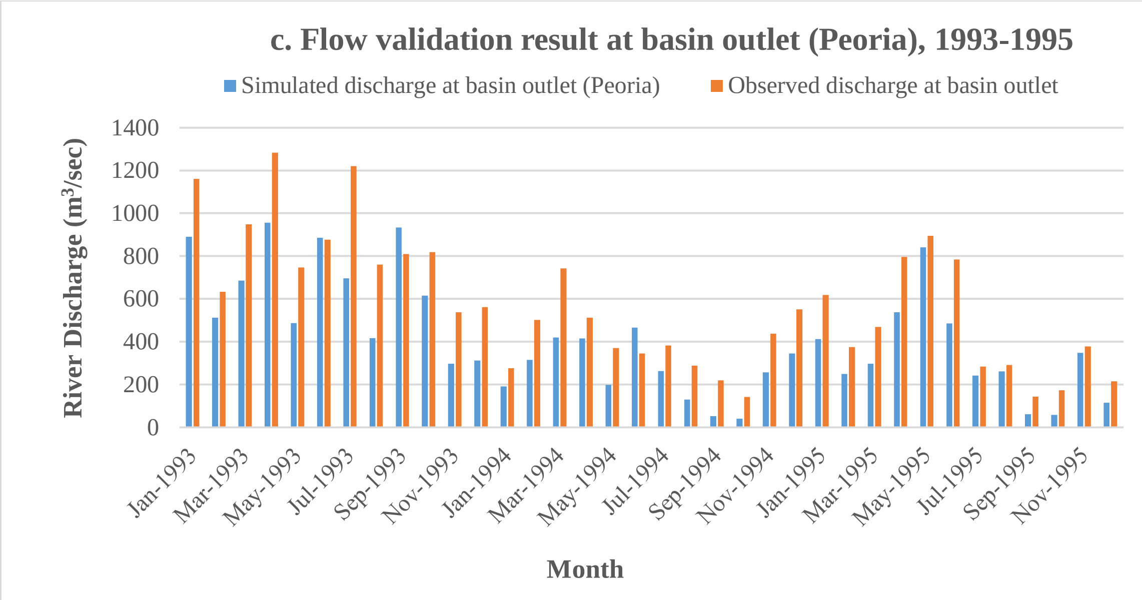


Figure 17 The distributions of land use in the UIRB. The inland area is also show. Land use map is modified from CDL 2008, Cropland Data Layer, National Agricultural Statistics Service. Basin outlet is at Peoria. 75% of the land use is agricultural, and urban land use accounts for about 17% of the total area. The inland area overlaps the Greater Chicago Area, where dominant land use is urban.


a. Flow calibration result at basin outlet (Peoria), 1996-2008
Simulated discharge at basin outlet (Peoria)
Observed discharge at basin outlet
River Discharge (m3/sec)
1400
1200
1000
800
600
400
200
0
Jan-1996
Jul-1996
Jan-1997
Jul-1997
Jan-1998
Jul-1998
Jan-1999
Jul-1999
Jan-2000
Jul-2000
Jan-2001
Jul-2001
Jan-2002
Jul-2002
Jan-2003
Jul-2003
Jan-2004
Jul-2004
Jan-2005
Jul-2005
Jan-2006
Jul-2006
Jan-2007
Jul-2007
Jan-2008
Jul-2008
Month


b. Flow calibration result at Marseilles, 1996-2008
Simulated discharge at Marseilles
Observed discharge at Marseilles
River Discharge (m3/sec)
900
800
700
600
500
400
300
200
100
0
Jan-1996
Jul-1996
Jan-1997
Jul-1997
Jan-1998
Jul-1998
Jan-1999
Jul-1999
Jan-2000
Jul-2000
Jan-2001
Jul-2001
Jan-2002
Jul-2002
Jan-2003
Jul-2003
Jan-2004
Jul-2004
Jan-2005
Jul-2005
Jan-2006
Jul-2006
Jan-2007
Jul-2007
Jan-2008
Jul-2008
Month



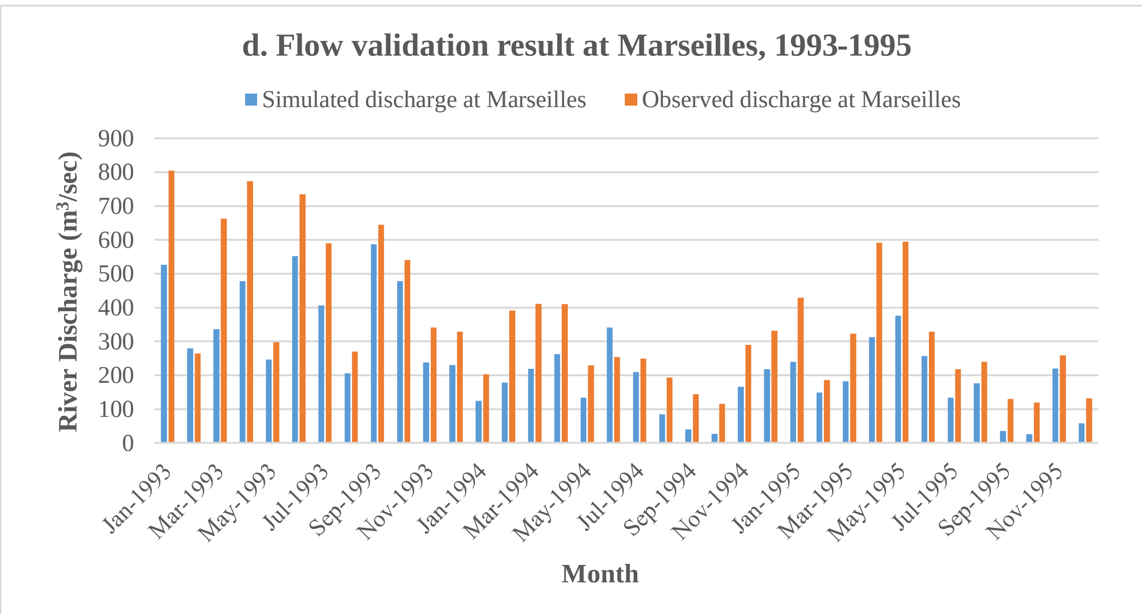


Figure 18 Flow calibration and validation results, respectively at basin outlet (Peoria) and Marseilles. Flow calibration was carried out for the period from 1996 to 2008 at both locations, and validation for the period from 1993 to 1995. Blue lines are SWAT simulated output of monthly discharge, while orange lines are observed monthly discharge at USGS gauges. The results of calibration and validation are excellent.

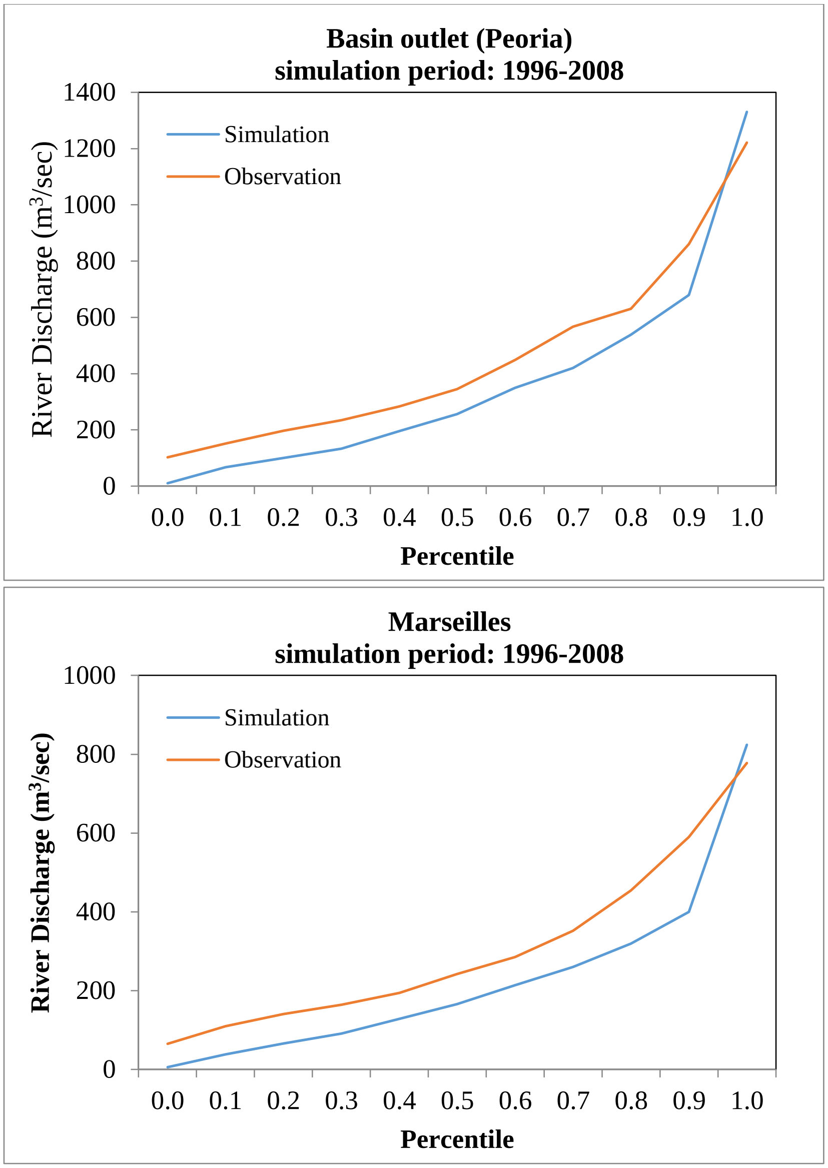
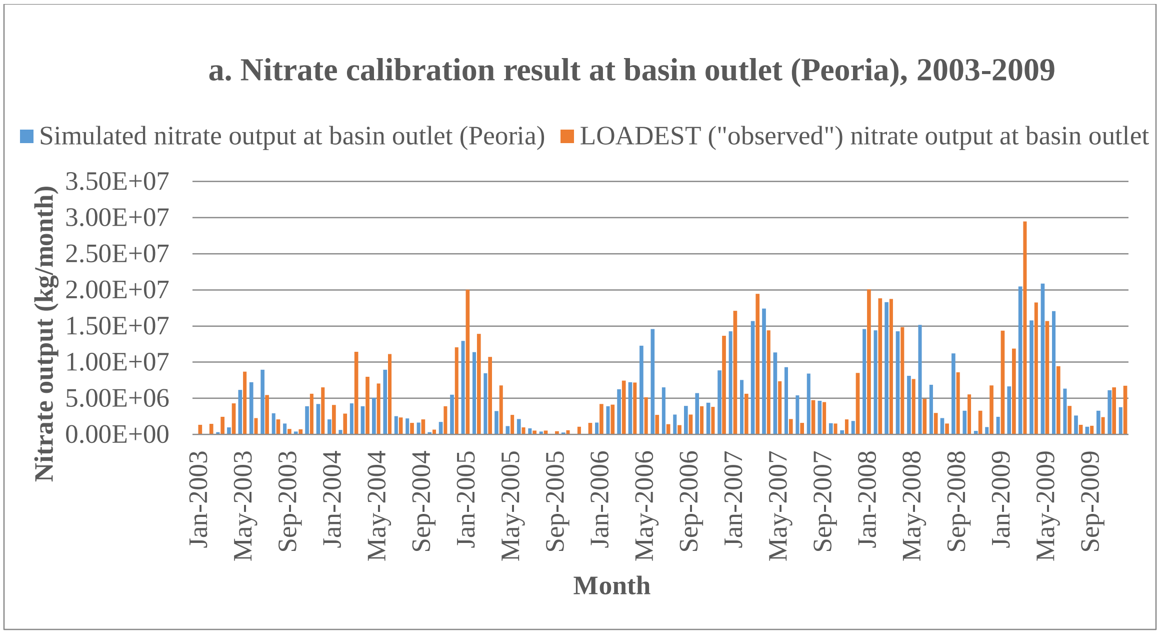
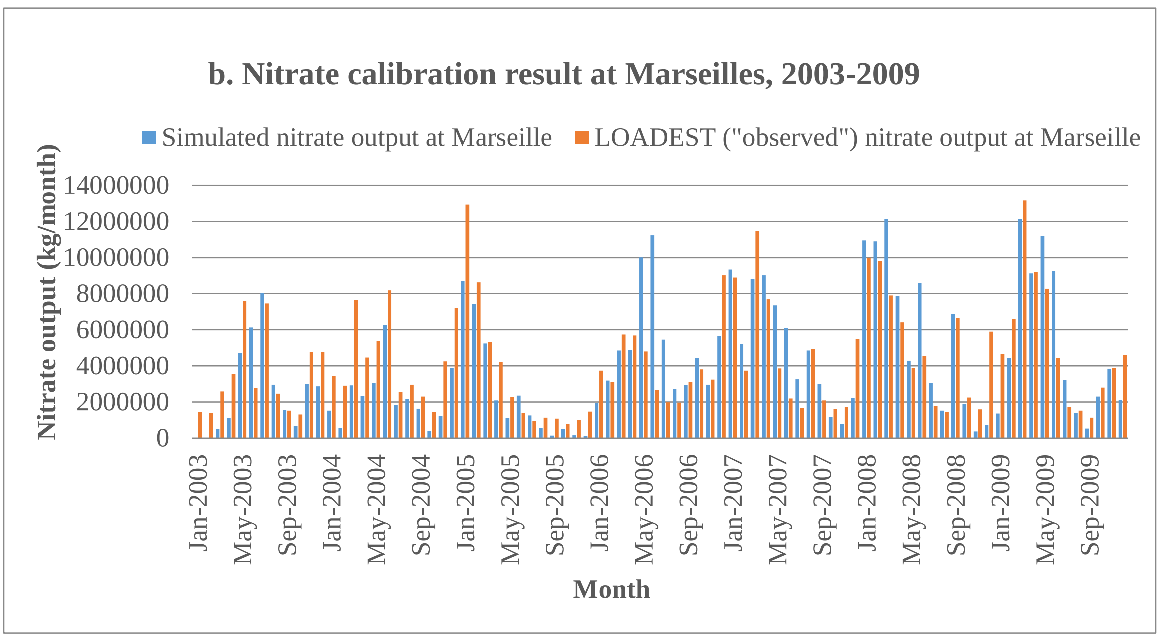
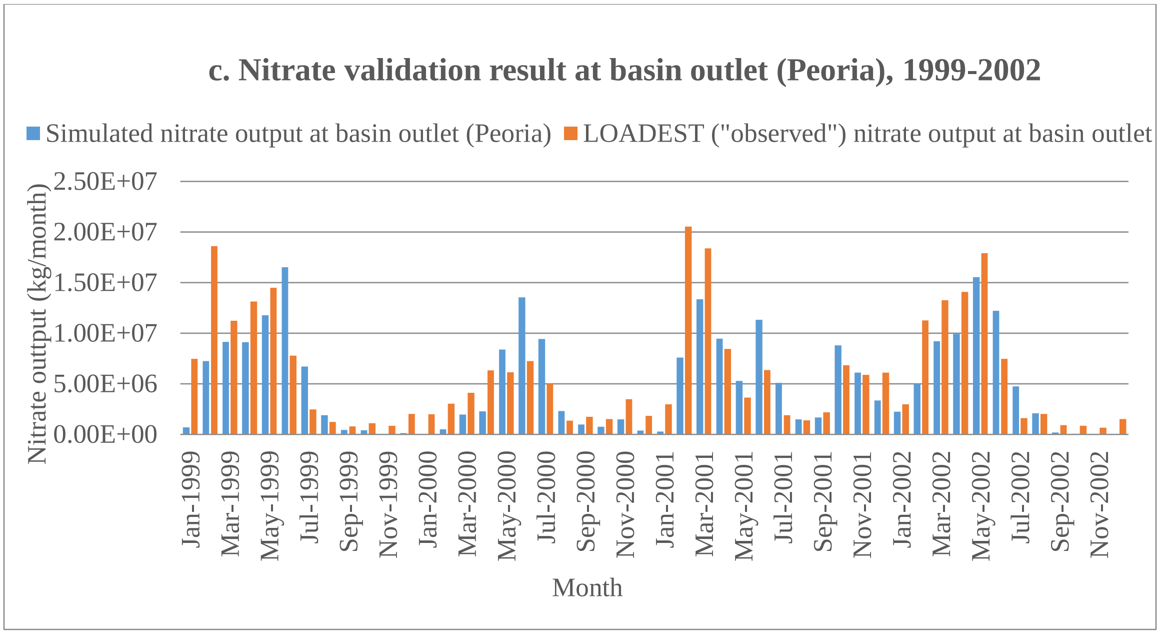


Figure 19 Cumulative distribution of monthly flows for the calibration period (1996-2008), at basin outlet (Peoria) and Marseilles. SWAT prediction of flow (blue) is lower than observation (orange). However, model is capable to predict extreme events (flood or drought).


a. Nitrate calibration result at basin outlet (Peoria), 2003-2009
Simulated nitrate output at basin outlet (Peoria)
LOADEST ("observed") nitrate output at basin outlet
Nitrate output (kg/month)
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
Jan-2003
May-2003
Sep-2003
Jan-2004
May-2004
Sep-2004
Jan-2005
May-2005
Sep-2005
Jan-2006
May-2006
Sep-2006
Jan-2007
May-2007
Sep-2007
Jan-2008
May-2008
Sep-2008
Jan-2009
May-2009
Sep-2009
Month


b. Nitrate calibration result at Marseilles, 2003-2009
Simulated nitrate output at Marseille
LOADEST ("observed") nitrate output at Marseille
Nitrate output (kg/month)
14000000
12000000
10000000
8000000
6000000
4000000
2000000
0
Jan-2003
May-2003
Sep-2003
Jan-2004
May-2004
Sep-2004
Jan-2005
May-2005
Sep-2005
Jan-2006
May-2006
Sep-2006
Jan-2007
May-2007
Sep-2007
Jan-2008
May-2008
Sep-2008
Jan-2009
May-2009
Sep-2009
Month



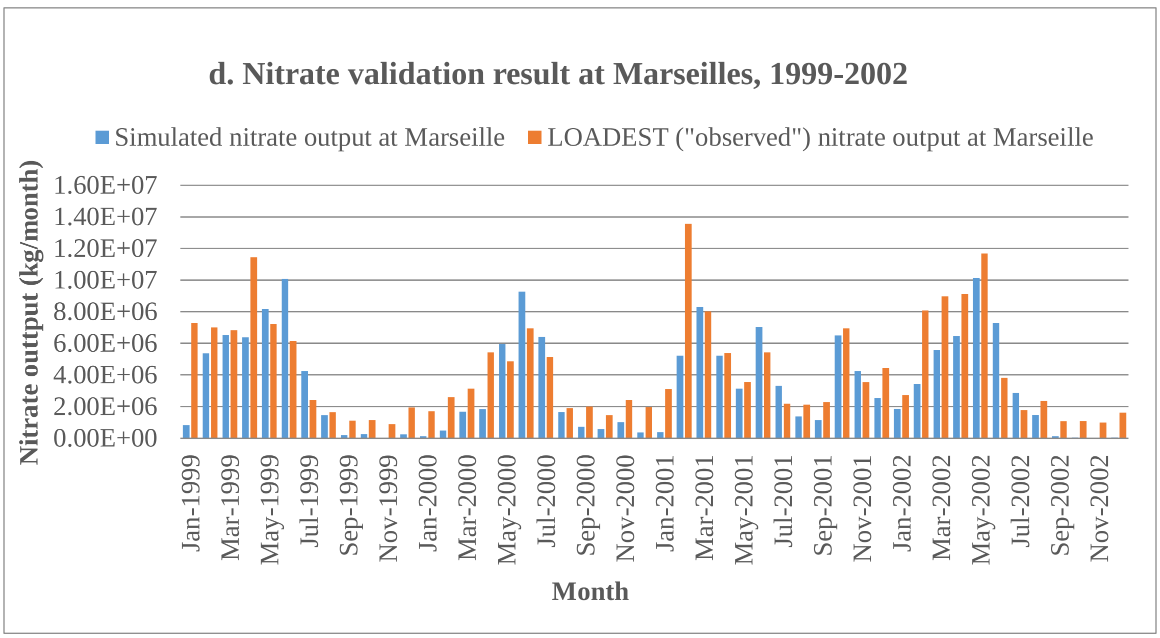


Figure 20 Nitrate calibration and validation results, respectively at basin outlet (Peoria) and Marseilles. Nitrate calibration was carried out for the period from 2003 to 2009 at both locations, and validation for the period from 1999 to 2002. Blue lines are monthly nitrate output simulated by SWAT, while orange lines are monthly nitrate output generated by Load Estimator (LOADEST) (Runkel et al., 2004), representing observed data. LOADEST estimation was based on existing daily measurements and statistical estimation method: Adjusted Maximum Likelihood Estimation. The results of calibration and validation are satisfactory.

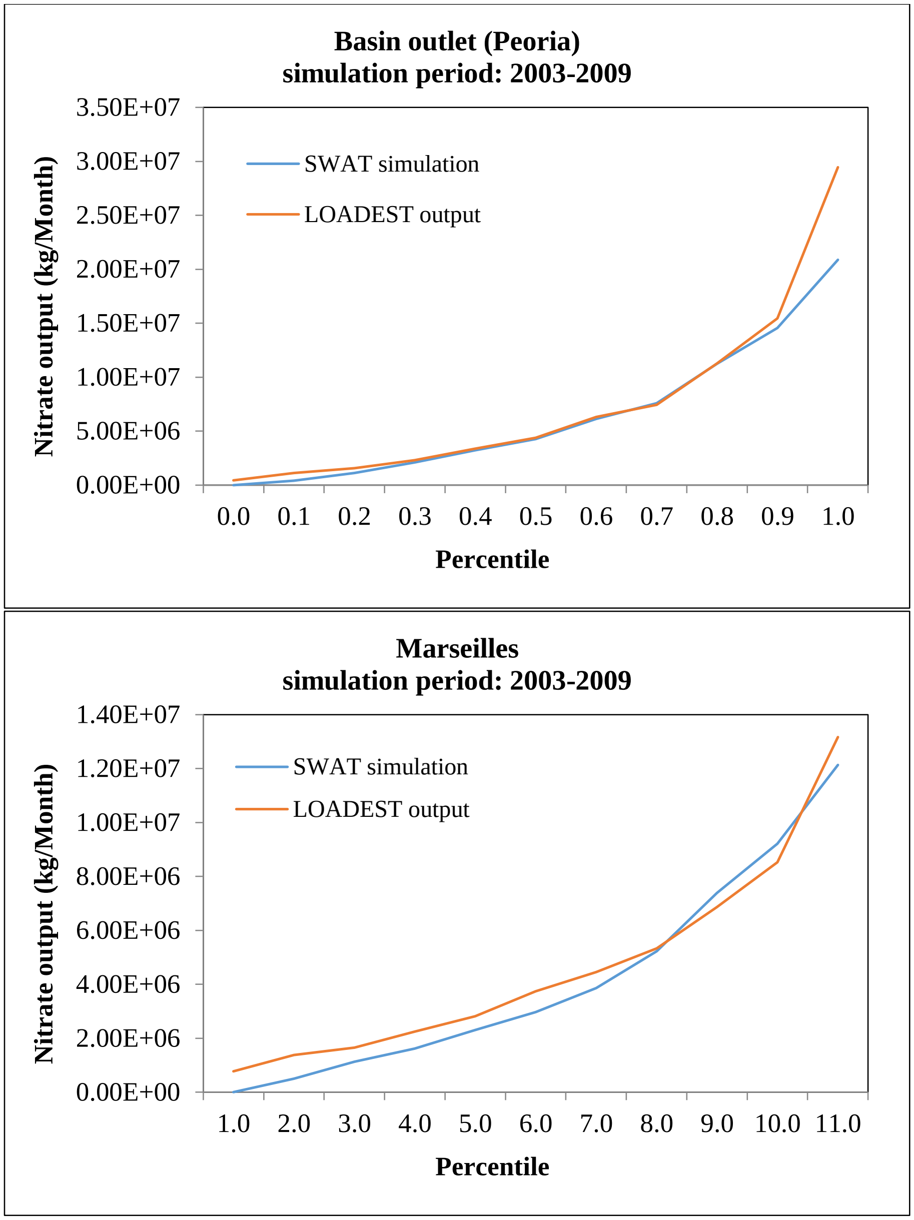
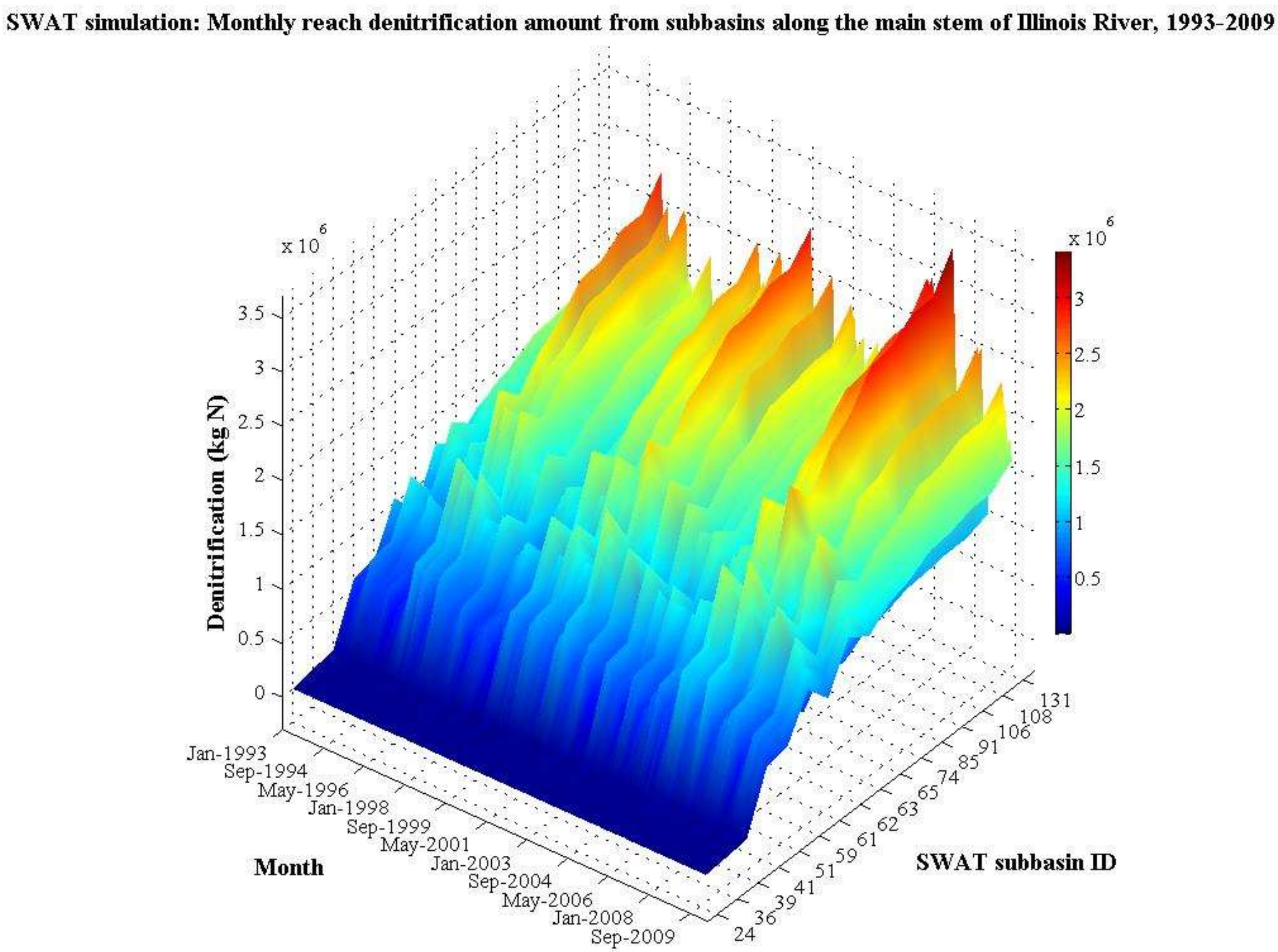
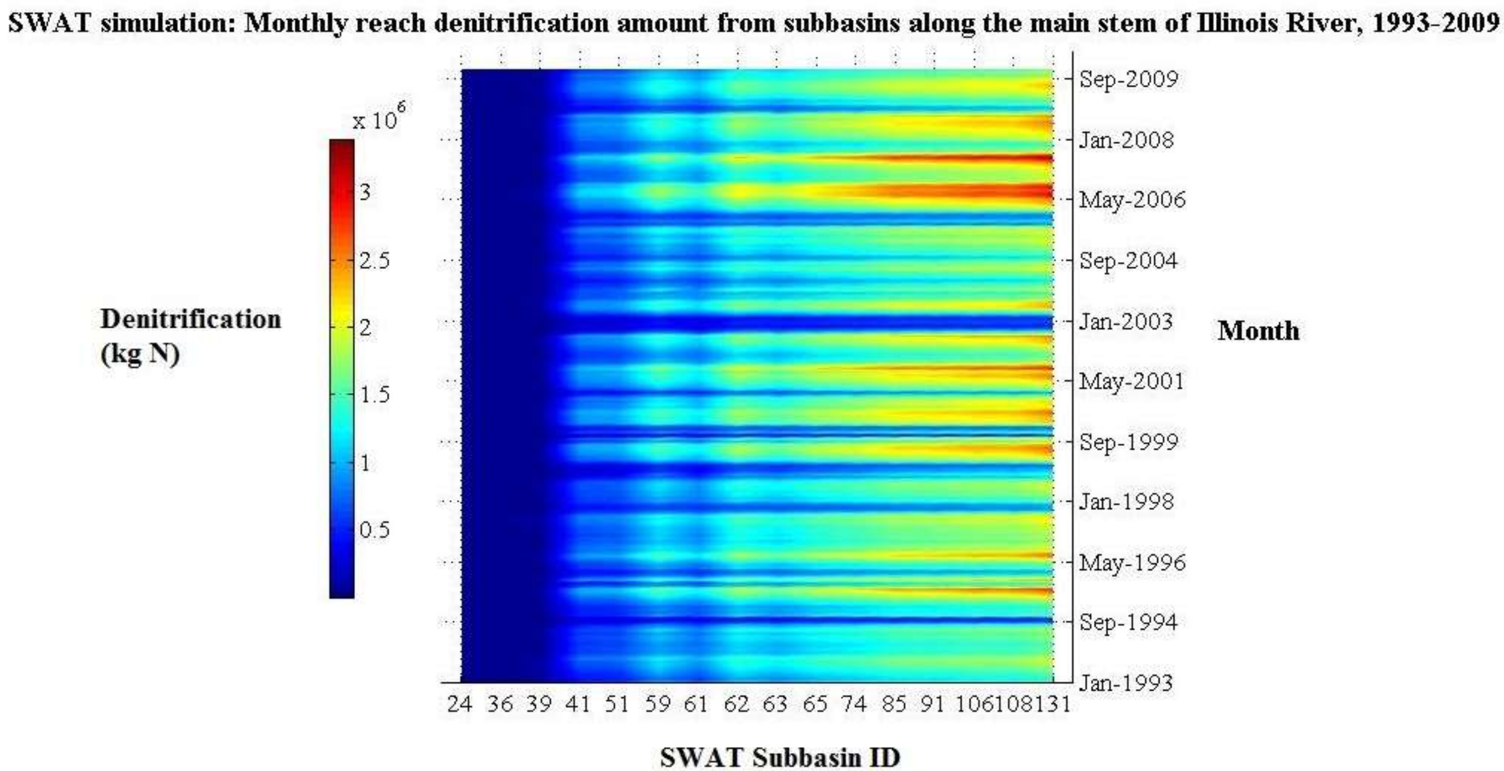


Figure 21 Cumulative distribution of monthly nitrate output for the calibration period (2003-2009), at basin outlet (Peoria) and Marseilles. SWAT simulation is able to predict


SWAT simulation: Monthly reach denitrification amount from subbasins along the main stem of Illinois River, 1993-2009
x 10^6
Denitrification (kg N)
0
0.5
1
1.5
2
2.5
3
3.5
x 10^6
0.5
1
1.5
2
2.5
3
Month
Jan-1993
Sep-1994
May-1996
Jan-1998
Sep-1999
May-2001
Jan-2003
Sep-2004
May-2006
Jan-2008
Sep-2009
SWAT subbasin ID
24
36
39
41
51
59
61
62
63
65
74
85
91
106
108
131

a:



b:

Figure 22 3-D plots of denitrification amount (kg N/month) calculated from SWAT simulation, 1993-2009. Monthly model output of nitrate from 16 subbasins located along the Illinois River main stem is plotted. Color bar demonstrates the intensity of denitrification: red represents high denitrification amount and dark blue represents little or no denitrification. a): indicates enhanced downstream denitrification on the Illinois River. Subbasin 24 is the most upstream subbasin, and subbasin 131 is at the UIRB basin outlet. An increasing trend of denitrification can be observed. b): A seasonal variation in denitrification can be observed, with elevated denitrification happening in July-September, and low denitrification in winter.

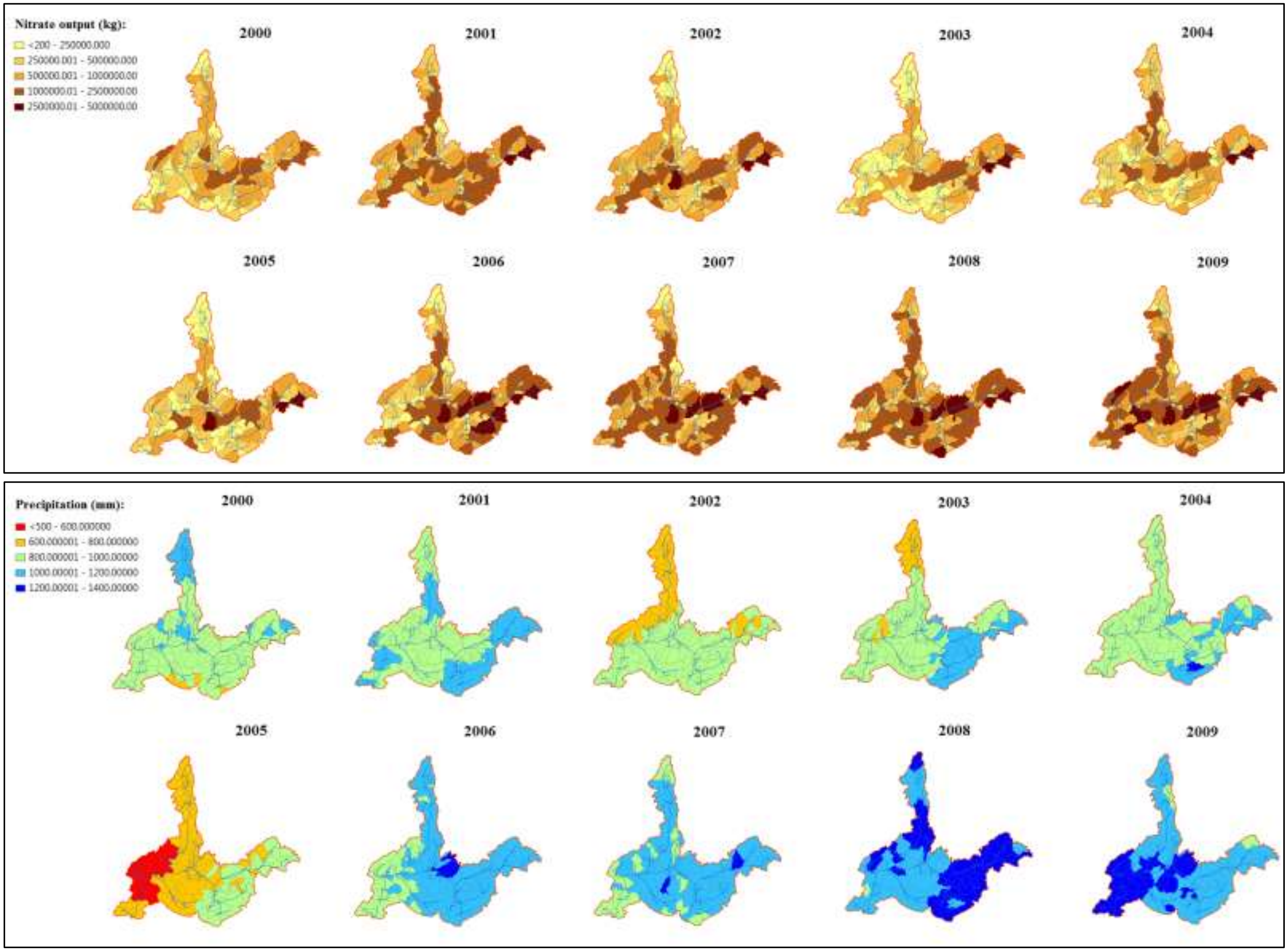


Figure 23 Annual NO_3 export (kg N) from 132 subbasins, 2000-2009 (above), and annual precipitation (mm) of each subbasin, 2000-2009. Plots demonstrate the control of hydrological conditions at the watershed scale. The NO_3 export values are generated from SWAT simulation results of nitrate output of each subbasin, while precipitation data are gauge measurements. At the basin scale, there is enhanced nitrate export during wet years (for example, 2008), and much less export during dry periods (for example, 2005). At the subbasin scale, a positive correlation between

precipitation and nitrate export is also observed: subbasins with higher precipitation have higher nitrate export; for the same subbasin, there is less nitrate exported in a dry year compared to a wet year.

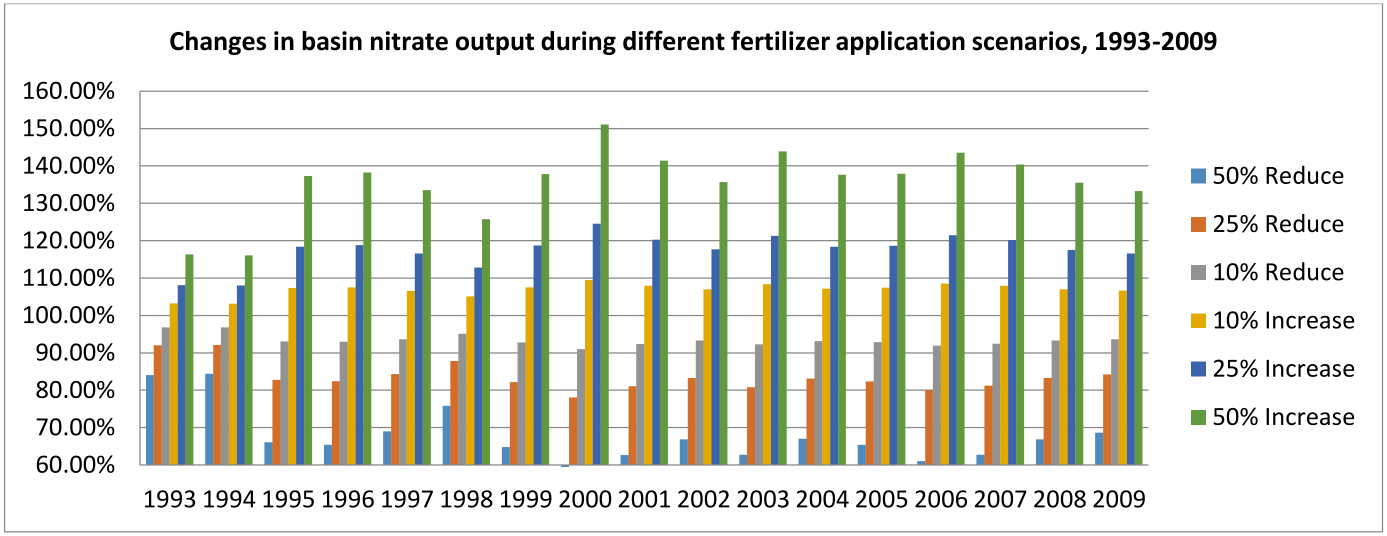


Figure 24. Percentage changes of simulated basin nitrate output (kg N) during different fertilizer application scenarios. Reducing the fertilizer application rate by 10%, 25%, and 50% can result in respectively 6%, 16%, and 31% reduction in nitrate export on the basin level at the end of the simulation (2009). Increasing the current SWAT fertilizer application rate by 10%, 25%, and 50% can cause an increase in basin nitrate export ranging from 3-10%, 8-25%, and 16-51% respectively during the entire simulation period.

TABLES

Table 2 Model input data sources for the Upper Illinois River Basin

Data Type	**Scale**	**Source**	**Description**
Topography	30m x 30m	USGS DEM (Digital Elevation Map)	Elevation, overland and channel slopes, lengths
Reach	-	USEPA RF1 (Reach File 1)	Pre-defined stream network; Defines subbasins
Soils	60m x 60m	STATSGO (State Soil Geographic Database)	Soil physical properties (e.g., bulk density, texture)
Land use	60m x 60m	USGS, 2001	National Land Cover Data for non-agricultural land classifications
Crop data layer	60m x 60m	CDL (Cropland Data Layer), 2008	Agricultural land classification

Weather stations	Subbasin level	NOAA National Climatic Data Center, 1990-2009	Daily temperature and precipitation
Land management	-	USDA National Agricultural Statistics Service, USDA Economic Research Service, USDA Economics, Statistics, and Market Information System	Fertilizer application rates and timing planting and harvesting information
Point sources	-	MWRDGC	Water quality of effluents of water reclamation plants

Table 3 SWAT parameter adjustments during model calibration. a. flow calibration (1996-2008); b. nitrate export calibration (1999-2004).

a. Flow calibration

Parameters	Definition	Initial value	Final value	Rank of sensitivity
CN2.hru	Initial runoff curve number for moisture condition II	Varies by HRUs	-1.85% (98.15% of initial value in the hru)	1
GWQMN.gw	Threshold depth of water in the shallow aquifer required for return flow to occur (mm H2O)	0	100	2
RCHRG_DP.gw	Deep aquifer percolation fraction	0.05	0.0056	3
ESCO.hru	Soil evaporation compensation factor	0	0.685	4
EPCO.hru	Plant uptake compensation factor	0	0.249	5
CANMX.hru	Maximum canopy storage (mmH2O)	0	9.634	6
TIMP.bsn	Snow pack temperature lag factor	1	0.065	7
ALPHA_BF.gw	Baseflow alpha factor (days)	0.048	0.950	8
CH_K.rte	Effective hydraulic conductivity in main channel alluvium (mm/hr)	0	112.4	9

SMTMP.bsn	Snow melt base temperature (℃)	0.5	-0.066	10

b. Nitrate calibration

Parameters	**Definition**	**Initial value**	**Final value**	**Rank of sensitivity**
CDN.bsn	Denitrification exponential rate coefficient	1.4	0.06	1
SDNCO.bsn	Denitrification threshold water content	1.1	0.99	2
N_UPDIS.bsn	Nitrogen uptake distribution parameter	20	100	3
CNYLD (crop.dat)	Normal fraction of nitrogen in yield (kg N/kg yield)	0.014 for corn	0.007 for corn	4
SURLAG.bsn	Surface runoff lag coefficient	4	24	5
FRT_SURFACE.mgt	Fraction of fertilizer applied to top 10mm of soil	0.2	0.95	6
HLIFE_NGW .gw /.bsn	Half-life of nitrate in the shallow aquifer (days)	0	500	7
FIXCO.bsn	Nitrogen fixation coefficient	0.5	0.8	8
NFIXMX.bsn	Maximum daily n-fixation (kg/ha)	10	20	9

NPERCO.bsn	Nitrate percolation coefficient	0.2	0.9	10
REVAPMN.gw	Threshold depth of water in the shallow aquifer required for percolation to the deep aquifer to occur (mm H2O)	1	300	11
RSDCO.bsn	Residue decomposition coefficient	0.05	0.5	12
SHALLST_N.gw	Initial concentration of nitrate in shallow aquifer	0	100	13
sol_NO3 (#1-10).chm	Initial nitrate concentration in the soil layer (mg N/kg soil or ppm)	0	20	14
sol_ORGN (#1-10).chm	Initial organic N concentration in the soil layer (mg N/kg soil or ppm)	0	20	15

CHAPTER 4

4. CONCLUSIONS AND SUMMARY

The combined studies of hydrologic modeling and isotopic/chemical measurements presented in this document provide a comprehensive perspective on understanding the nitrate delivery mechanisms and controlling factors within the UIRB.

The measurements of stream nitrate demonstrate the seasonal variations in nitrate concentrations and isotopic values. The "spring flush" event, represented by high spring nitrate concentration in river samples happens from March to April, subsides in June, and minimizes in September and October. Both SWAT modeling and in-situ measurements show high nitrate flux in spring and low nitrate flux in later fall to winter. The seasonality in N flux and concentration is due to combined effect of high fertilizer application rate and precipitation intensity in spring, which leads to enhanced nitrate input to stream from soil leaching and tile drainage. Spring data of nitrate isotopes resemble a mixture of soil N and nitrified reduced-N fertilizer.

The calculated N yield from major tributaries shows that urban area of Chicago has relative constant nitrate input in both fall and spring, while agricultural watersheds have fall yields of nitrate less than 10% of that of spring. The rapid decease is caused by lack of direct surface input and enhanced nitrate removal by plant uptake and denitrification.

The seasonal variation in isotopic compositions is evidence of two dominant sources of nitrate within the UIRB: the treated wastewater effluents and agricultural input. Nitrate derived from fertilizer and soil N has higher $\delta^{18}O$ values and lower $\delta^{15}N$ values compared to nitrate derived from effluets of wastewater treatment plants. Isotopic values of spring stream nitrate of the Illinois River and some major tributaries are close to that of spring drainage tile and shallow groundwater samples from Illinois, showing that tile drainage and agricultural input is the primary source of stream nitrate export in spring. Compared to agricultural source, both nitrate concentration and isotopic values of WTP effluents stay relatively constant year round.

The land use effect on basin nitrate is evident also by the spatial variations in isotopic and chemical values along the waterway. The downstream portion of the Upper Illinois River, which is dominated by agricultural land, has higher nitrate concentration than the upstream portion—mostly urbanized area—in the spring and the converse occurs in summer and fall. Tributary inputs have great impact on overall basin nitrate export. Land use patterns are reflected in isotopic data. Isotopic compositions of nitrate in tributaries draining agricultural subbasins define an apparent denitrification trend with $\delta^{15}N$ and $\delta^{18}O$ values increasing as nitrate concentrations decrease from spring through fall. The trend is also observable in tributaries having mixed urban-agricultural land use, but less so in those dominated by urban land use where WTP effluent is the dominant source of river nitrate.

Meteorological conditions have a strong impact on nitrate export, which is evident from both isotopic and modeling studies. Annual basin nitrate export calculated from SWAT simulation exhibits positive correlation with precipitation at both basin and subbasin scales. The variation in precipitation amount is reflected in the spatial variation of subbasin NO_3^- loads: areas with relatively intense rainfalls have higher nitrate output, and individual subbasins can behave differently under different meteorological conditions. The profound impact of precipitation is due to its control of stream discharge, water depth, and stream velocity, as well as its role in driving tile drainage and soil leaching processes within the basin.

SWAT simulation with unprecedented stream-denitrification implementation demonstrates the cumulative amount of denitrification along the Illinois River waterway. The aggregate denitrification effect is revealed by increasing amount of denitrification downstream over 17 simulated years. A seasonal pattern in denitrification at the basin scale is also observed from SWAT results. The maximum in-stream denitrification occurred during late summer to fall, from June to September, and the least denitrification occurred during winter to spring. The temporal changes were mostly in response to changing weather and stream flow. The dry season with low discharge, stream depth, and velocity provides the optimum conditions for denitrification, since in-stream denitrification occurs mainly in benthic sediments. Through regulating the nitrate removal processes, precipitation has great impact on controlling basin nutrient output.

Both approaches show that denitrification is a dominant process in summer and fall within the UIRB. It is indicated by the elevated $\delta^{15}N$ and $\delta^{18}O$ values evolving along the denitrification trajectory. The Illinois River is a mixture of urban treated wastewater and denitrified agricultural input. The O/N isotopic enrichment factor ratio for denitrification is 0.79, falling within the expected interval between 0.5 and 1.0.

SWAT simulation of land use (fertilizer application) scenarios provides insight into nutrient management. The simulations show that changes in fertilizer application can cause significant changes in basin nitrate export in the UIRB, applying SWAT2009 version with stream denitrification implemented. Increasing fertilizer application rate does not lead to proportional corn production enhancement, however, can lead to significant changes in nitrate export and cause severe environmental issues. More scientific management plans need to be made in order to achieve the biofuel production goal without hampering the nitrate reduction target.

The studies of hydrological modeling and measurements of river nitrate concentration and isotopic compositions of the UIRB have demonstrated their powerful applications for us to better understand nitrate source distribution, mixing mechanisms, and in-stream processes. Both approaches were applied to study land use impact on nitrate export and have yielded significant results that can assist people to establish better land use management plans and nitrate reduction strategies.

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APPENDICES

Table 4 N data of sampling programs 1, 2, and 3

(Category: 1=SWRP, 2-Illinois River Waterway, 3-urban tributaries, 4=mixed tributaries, 5-agricultural tributaries, 6-shallow groundwater)

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N-NO_3$	$\delta^{18}O-NO_3$	NO_3-N (mg/L)
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	10/19/2004	7.82	0.1	12.38
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	3/22/2005	9.75	3.26	13.58
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	4/14/2005	8.08	2.10	6.83
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	4/29/2005	8.3	3.12	10.23
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	6/13/2005	10.45	2.99	11.46
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	7/13/2005	7.4	0.83	7.82
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	8/1/2005	7.64	0.41	10.43
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	9/13/2005	8.03	-0.35	7.22
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	10/3/2005	6.99	0.17	10.94
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	11/1/2005	8.98	-1.00	6.82
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	3/29/2006	9.25	2.41	8.61
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	4/19/2006	8.7	2.23	6.76
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	5/1/2006	6.79	1.78	4.92
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	6/20/2006	10.11	0.99	6.55
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	7/19/2006	5.82	-0.08	6.17
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	8/7/2006	7.21	0.1	8.56
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	9/21/2006	10.45	0.37	9.39
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	10/2/2006	9.03	0.47	11.58
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	3/25/2008	4.26	-0.27	5.97
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	4/22/2008	11.25	2.36	11.56
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	5/20/2008	9.96	1.85	10.61
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	6/17/2008	10.9	1.78	10.47

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N-NO_3$	$\delta^{18}O-NO_3$	NO_3-N (mg/L)
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	7/15/2008	10.03	1.99	9.79
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	9/9/2008	9.52	-2.09	5.1
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	9/30/2008	7.63	-1.66	5.58
1	SWRP	Stickney Wastewater Reclamation Plant	41.8172	-87.7660	10/22/2008	9.5	-1.12	9.4
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	10/15/2004	8.65	0.27	7.17
2	2	Chicago Sanitary and Ship Canal, ILWW 290.5	41.5595	-88.0776	10/15/2004	8.86	0.52	7.18
2	3	Des Plaines River, ILWW Mile 287.3	41.5174	-88.0883	10/15/2004	9.16	0.41	7.43
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	10/15/2004	9.23	0.34	7.5
2	5	Des Plaines River, ILWW Mile 285.0	41.4945	-88.1193	10/15/2004	9.27	0.43	7.12
2	6	Des Plaines River, ILWW Mile 282.8	41.4742	-88.1483	10/15/2004	9.23	0.64	7.18
2	7	Des Plaines River, ILWW Mile 280.5	41.4530	-88.1661	10/15/2004	9.16	0.75	7.41
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	10/15/2004	10.6	0.91	7.91
2	9	Des Plaines River, ILWW Mile 276.1	41.4047	-88.2180	10/15/2004	9.85	1.2	7.92
2	10	Des Plaines River, ILWW Mile 274.0	41.3829	-88.2423	10/14/2004	10.22	1.34	8.09
2	11	Illinois River, ILWW Mile 272.4	41.3992	-88.2650	10/14/2004	10.54	1.68	6.79
2	12	Illinois River, ILWW Mile 270.0	41.3920	-88.3103	10/14/2004	10.97	2.37	4.68
2	13	Illinois River, ILWW Mile 276.8	41.3786	-88.3401	10/14/2004	11.12	2.97	4.4
2	14	Illinois River, ILWW Mile 265.0	41.3615	-88.3948	10/14/2004	11.1	2.73	4.31
2	15	Illinois River, ILWW Mile 263.0	41.3530	-88.4298	10/14/2004	11.07	2.32	4.75
2	16	Illinois River, ILWW Mile 261.6	41.3476	-88.4562	10/14/2004	10.91	2.55	4.59
2	17	Illinois River, ILWW Mile 256.0	41.3227	-88.5552	10/14/2004	10.69	2.74	4.69
2	18	Illinois River, ILWW Mile 253.0	41.2990	-88.6044	10/14/2004	10.47	2.44	4.36
2	19	Illinois River, ILWW Mile 250.0	41.3139	-88.6549	10/14/2004	10.91	2.21	4.51
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	10/14/2004	10.87	2.26	4.6
2	21	Illinois River, ILWW Mile 246.0	41.3251	-88.7243	10/14/2004	10.52	1.91	4.78
2	22	Illinois River, ILWW Mile 243.7	41.3322	-88.7693	10/14/2004	10.59	2.01	4.7
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	10/14/2004	10.56	1.95	4.75

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data $\delta^{15}N-NO_3$	$\delta^{18}O-NO_3$	NO_3-N (mg/L)
2	24	Illinois River, ILWW Mile 238.5	41.3362	-88.8642	10/14/2004	10.84	2.17	4.02
2	25	Illinois River, ILWW Mile 236.8	41.3224	-88.8800	10/14/2004	10.66	1.69	4.35
2	26	Illinois River, ILWW Mile 234.5	41.3189	-88.9238	10/14/2004	10.82	2.19	4.22
2	27	Illinois River, ILWW Mile 231.7	41.3215	-88.9771	10/13/2004	11.47	2.9	4.32
2	28	Illinois River, ILWW Mile 229.6	41.3276	-89.0100	10/13/2004	11.65	3.09	4.29
2	29	Illinois River, ILWW Mile 226.9	41.3205	-89.0644	10/13/2004	11.64	2.82	4.58
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	10/13/2004	11.81	3.05	4.37
2	31	Illinois River, ILWW Mile 222.6	41.3233	-89.1241	10/13/2004	11.68	2.45	4.31
2	32	Illinois River, ILWW Mile 219.8	41.3084	-89.1709	10/13/2004	11.97	2.88	4.04
2	33	Illinois River, ILWW Mile 217.1	41.3136	-89.2253	10/13/2004	11.87	2.8	3.96
2	34	Illinois River, ILWW Mile 213.4	41.3136	-89.2819	10/13/2004	11.67	3.1	3.91
2	35	Illinois River, ILWW Mile 209.4	41.2820	-89.3370	10/13/2004	11.98	3.22	3.79
2	36	Illinois River, ILWW Mile 205.0	41.2220	-89.3588	10/13/2004	12.04	3.04	3.85
2	37	Illinois River, ILWW Mile 200.4	41.1619	-89.3193	10/13/2004	11.8	3.14	3.77
2	38	Illinois River, ILWW Mile 196.9	41.1159	-89.3365	10/13/2004	11.7	3.1	3.47
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	10/13/2004	11.61	3.36	3.17
2	40	Illinois River, ILWW Mile 186.4	40.9878	-89.4385	10/13/2004	11.97	3.67	2.91
2	41	Illinois River, ILWW Mile 183.2	40.9499	-89.4540	10/13/2004	11.85	3.71	2.79
2	42	Illinois River, ILWW Mile 179.0	40.8941	-89.4906	10/13/2004	12.13	3.79	2.56
2	43	Illinois River, ILWW Mile 174.9	40.8410	-89.5242	10/12/2004	12.66	4.62	2.53
2	44	Illinois River, ILWW Mile 170.9	40.7127	-89.5475	10/12/2004	12.69	4.61	2.25
2	45	Illinois River, ILWW Mile 165.3	40.6891	-89.5833	10/12/2004	13.84	5.69	1.7
2	46	Illinois River, ILWW Mile 162.8	40.6684	-89.6110	10/12/2004	13.7	5.5	1.56
2	47	Illinois River, ILWW Mile 160.6	40.6684	-89.6110	10/12/2004	13.39	5.35	1.61
2	48	Illinois River, ILWW Mile 159.4	40.6510	-89.6099	10/12/2004	13.72	5.09	1.65
2	49	Illinois River, ILWW Mile 158.2	40.6393	-89.6183	10/12/2004	13.5	5.42	1.61
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	4/13/2005	10.02	2.52	8.19
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	4/13/2005	9.42	2.88	6.63

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						δ^{15}N-NO_3	δ^{18}O-NO_3	NO_3-N (mg/L)
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	4/13/2005	8.84	2.46	6.11
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	4/12/2005	9.16	4.09	3.84
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	4/12/2005	8.69	3.56	3.66
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	4/12/2005	9.47	4.57	3.66
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	4/12/2005	8.35	4.73	4.10
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	5/2/2005	9.71	2.34	7.3
2	2	Chicago Sanitary and Ship Canal, ILWW 290.5	41.5595	-88.0776	5/2/2005	10.02	2.65	7.21
2	3	Des Plaines River, ILWW Mile 287.3	41.5174	-88.0883	5/2/2005	10.48	2.38	6.68
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	5/2/2005	9.83	2.11	6.61
2	5	Des Plaines River, ILWW Mile 285.0	41.4945	-88.1193	5/2/2005	10.03	2.07	6.65
2	6	Des Plaines River, ILWW Mile 282.8	41.4742	-88.1483	5/2/2005	9.86	2.93	7.32
2	7	Des Plaines River, ILWW Mile 280.5	41.4530	-88.1661	5/2/2005	10.22	3.08	7.62
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	5/2/2005	9.56	2.52	6.98
2	9	Des Plaines River, ILWW Mile 276.1	41.4047	-88.2180	5/2/2005	10.2	2.32	6.62
2	10	Des Plaines River, ILWW Mile 274.0	41.3829	-88.2423	5/3/2005	10.14	2.43	6.53
2	11	Illinois River, ILWW Mile 272.4	41.3992	-88.2650	5/3/2005	9.93	3.47	5.43
2	12	Illinois River, ILWW Mile 270.0	41.3920	-88.3103	5/3/2005	10.17	3.84	4.88
2	13	Illinois River, ILWW Mile 276.8	41.3786	-88.3401	5/3/2005	9.06	4.31	4.83
2	14	Illinois River, ILWW Mile 265.0	41.3615	-88.3948	5/3/2005	9.7	3.81	5.2
2	15	Illinois River, ILWW Mile 263.0	41.3530	-88.4298	5/3/2005	9.5	3.98	5.33
2	16	Illinois River, ILWW Mile 261.6	41.3476	-88.4562	5/3/2005	9.39	4.1	5.44
2	17	Illinois River, ILWW Mile 256.0	41.3227	-88.5552	5/3/2005	9.22	3.58	5.45
2	18	Illinois River, ILWW Mile 253.0	41.2990	-88.6044	5/3/2005	9.3	4.2	5.37
2	19	Illinois River, ILWW Mile 250.0	41.3139	-88.6549	5/3/2005	9.42	4.55	5.39
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	5/3/2005	9.57	4.1	5.46
2	21	Illinois River, ILWW Mile 246.0	41.3251	-88.7243	5/3/2005	8.42	4.42	5.44
2	22	Illinois River, ILWW Mile 243.7	41.3322	-88.7693	5/3/2005	9.48	4.32	5.52

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N-NO_3$	$\delta^{18}O-NO_3$	NO_3-N (mg/L)
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	5/3/2005	8.92	4.4	5.38
2	24	Illinois River, ILWW Mile 238.5	41.3362	-88.8642	5/3/2005	8.94	4.71	4.61
2	25	Illinois River, ILWW Mile 236.8	41.3224	-88.8800	5/3/2005	8.94	4.47	4.9
2	26	Illinois River, ILWW Mile 234.5	41.3189	-88.9238	5/3/2005	8.88	4.64	5.02
2	27	Illinois River, ILWW Mile 231.7	41.3215	-88.9771	5/4/2005	9.1	4.44	4.71
2	28	Illinois River, ILWW Mile 229.6	41.3276	-89.0100	5/4/2005	9.4	4.81	4.7
2	29	Illinois River, ILWW Mile 226.9	41.3205	-89.0644	5/4/2005	8.82	4.96	4.73
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	5/4/2005	8.9	4.88	4.91
2	31	Illinois River, ILWW Mile 222.6	41.3233	-89.1241	5/4/2005	8.11	5.03	5.69
2	32	Illinois River, ILWW Mile 219.8	41.3084	-89.1709	5/4/2005	8.62	5.82	5.63
2	33	Illinois River, ILWW Mile 217.1	41.3136	-89.2253	5/4/2005	7.89	4.96	5.42
2	34	Illinois River, ILWW Mile 213.4	41.3136	-89.2819	5/4/2005	8.47	5.1	5.76
2	35	Illinois River, ILWW Mile 209.4	41.2820	-89.3370	5/4/2005	8.77	5.31	5.66
2	36	Illinois River, ILWW Mile 205.0	41.2220	-89.3588	5/4/2005	8.91	5.33	5.62
2	37	Illinois River, ILWW Mile 200.4	41.1619	-89.3193	5/4/2005	8.8	5.02	5.64
2	38	Illinois River, ILWW Mile 196.9	41.1159	-89.3365	5/4/2005	9.14	5.6	5.6
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	5/4/2005	8.67	5.48	5.86
2	40	Illinois River, ILWW Mile 186.4	40.9878	-89.4385	5/4/2005	9.01	5.35	5.97
2	41	Illinois River, ILWW Mile 183.2	40.9499	-89.4540	5/4/2005	9.2	5.27	5.58
2	42	Illinois River, ILWW Mile 179.0	40.8941	-89.4906	5/4/2005	8.76	5.64	5.8
2	43	Illinois River, ILWW Mile 174.9	40.8410	-89.5242	5/5/2005	8.97	5.7	5.63
2	44	Illinois River, ILWW Mile 170.9	40.7127	-89.5475	5/5/2005	9.25	5.65	5.33
2	45	Illinois River, ILWW Mile 165.3	40.6891	-89.5833	5/5/2005	9.24	5.94	5.18
2	46	Illinois River, ILWW Mile 162.8	40.6684	-89.6110	5/5/2005	9.3	5.8	5.11
2	47	Illinois River, ILWW Mile 160.6	40.6684	-89.6110	5/5/2005	9.19	6.17	5.15
2	48	Illinois River, ILWW Mile 159.4	40.6510	-89.6099	5/5/2005	9.56	6.37	5.18
2	49	Illinois River, ILWW Mile 158.2	40.6393	-89.6183	5/5/2005	8.89	6.49	5.23
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	6/15/2005	11.22	2.92	4.54

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N-NO_3$	$\delta^{18}O-NO_3$	NO_3-N (mg/L)
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	6/15/2005	12.20	3.18	4.72
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	6/15/2005	12.45	2.90	5.00
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	6/14/2005	12.62	4.69	2.41
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	6/14/2005	12.95	4.36	3.55
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	6/14/2005	12.52	5.24	2.99
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	6/14/2005	13.20	5.73	2.71
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	7/13/2005	10.04	1.77	5.22
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	7/13/2005	10.99	1.70	5.30
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	7/13/2005	11.62	1.92	4.94
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	7/12/2005	12.80	3.14	3.25
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	7/12/2005	13.23	3.20	3.07
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	7/12/2005	14.68	4.97	2.20
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	7/12/2005	14.66	5.75	1.90
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	8/1/2005	7.73	0.87	5.11
2	2	Chicago Sanitary and Ship Canal, ILWW 290.5	41.5595	-88.0776	8/1/2005	7.63	1.12	5.24
2	3	Des Plaines River, ILWW Mile 287.3	41.5174	-88.0883	8/1/2005	7.86	1.21	5.35
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	8/1/2005	8.5	1.18	5.26
2	5	Des Plaines River, ILWW Mile 285.0	41.4945	-88.1193	8/1/2005	9.22	1.64	5.32
2	6	Des Plaines River, ILWW Mile 282.8	41.4742	-88.1483	8/1/2005	8.37	0.75	5.31
2	7	Des Plaines River, ILWW Mile 280.5	41.4530	-88.1661	8/1/2005	8.66	0.9	5.58
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	8/1/2005	9.97	0.79	5.04
2	9	Des Plaines River, ILWW Mile 276.1	41.4047	-88.2180	8/1/2005	10.64	1.57	4.56
2	10	Des Plaines River, ILWW Mile 274.0	41.3829	-88.2423	8/2/2005	10.56	1.81	4.35
2	11	Illinois River, ILWW Mile 272.4	41.3992	-88.2650	8/2/2005	10.67	3.31	3.11
2	12	Illinois River, ILWW Mile 270.0	41.3920	-88.3103	8/2/2005	10.48	2.78	3.3
2	13	Illinois River, ILWW Mile 276.8	41.3786	-88.3401	8/2/2005	10.8	2.86	3.42
2	14	Illinois River, ILWW Mile 265.0	41.3615	-88.3948	8/2/2005	10.52	2.24	3.78

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N\text{-}NO_3$	$\delta^{18}O\text{-}NO_3$	$NO_3\text{-}N$ (mg/L)
2	15	Illinois River, ILWW Mile 263.0	41.3530	-88.4298	8/2/2005	11.12	3.15	3.67
2	16	Illinois River, ILWW Mile 261.6	41.3476	-88.4562	8/2/2005	10.8	2.49	3.52
2	17	Illinois River, ILWW Mile 256.0	41.3227	-88.5552	8/2/2005	10.77	2.21	3.03
2	18	Illinois River, ILWW Mile 253.0	41.2990	-88.6044	8/2/2005	11.23	2.4	3.16
2	19	Illinois River, ILWW Mile 250.0	41.3139	-88.6549	8/2/2005	10.92	2.28	3.03
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	8/2/2005	10.98	2.69	2.95
2	21	Illinois River, ILWW Mile 246.0	41.3251	-88.7243	8/2/2005	11.04	2.85	3.02
2	22	Illinois River, ILWW Mile 243.7	41.3322	-88.7693	8/2/2005	11.04	2.75	3.06
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	8/2/2005	11.43	2.82	2.99
2	24	Illinois River, ILWW Mile 238.5	41.3362	-88.8642	8/2/2005	11.29	2.88	2.55
2	25	Illinois River, ILWW Mile 236.8	41.3224	-88.8800	8/2/2005	11.54	3.28	2.54
2	26	Illinois River, ILWW Mile 234.5	41.3189	-88.9238	8/2/2005	11.74	2.81	2.62
2	27	Illinois River, ILWW Mile 231.7	41.3215	-88.9771	8/3/2005	11.14	2.73	2.63
2	28	Illinois River, ILWW Mile 229.6	41.3276	-89.0100	8/3/2005	11.63	3.2	2.69
2	29	Illinois River, ILWW Mile 226.9	41.3205	-89.0644	8/3/2005	11.71	3.13	2.77
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	8/3/2005	12.02	3.05	2.73
2	31	Illinois River, ILWW Mile 222.6	41.3233	-89.1241	8/3/2005	12.06	3.39	2.79
2	32	Illinois River, ILWW Mile 219.8	41.3084	-89.1709	8/3/2005	11.94	3.08	2.87
2	33	Illinois River, ILWW Mile 217.1	41.3136	-89.2253	8/3/2005	11.95	3.32	2.55
2	34	Illinois River, ILWW Mile 213.4	41.3136	-89.2819	8/3/2005	12.19	3.2	2.57
2	35	Illinois River, ILWW Mile 209.4	41.2820	-89.3370	8/3/2005	12.03	3.18	2.62
2	36	Illinois River, ILWW Mile 205.0	41.2220	-89.3588	8/3/2005	12.48	3.71	2.63
2	37	Illinois River, ILWW Mile 200.4	41.1619	-89.3193	8/3/2005	12.26	3.53	2.57
2	38	Illinois River, ILWW Mile 196.9	41.1159	-89.3365	8/3/2005	12.42	3.87	2.68
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	8/3/2005	12.6	3.78	2.55
2	40	Illinois River, ILWW Mile 186.4	40.9878	-89.4385	8/3/2005	12.57	4.2	2.33
2	41	Illinois River, ILWW Mile 183.2	40.9499	-89.4540	8/3/2005	12.67	4.19	2.22
2	42	Illinois River, ILWW Mile 179.0	40.8941	-89.4906	8/3/2005	12.6	3.93	1.94
2	43	Illinois River, ILWW Mile 174.9	40.8410	-89.5242	8/4/2005	13.43	4.74	1.91

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N-NO_3$	$\delta^{18}O-NO_3$	NO_3-N (mg/L)
2	44	Illinois River, ILWW Mile 170.9	40.7127	-89.5475	8/4/2005	14.18	5.59	1.54
2	45	Illinois River, ILWW Mile 165.3	40.6891	-89.5833	8/4/2005	15.54	7.03	1.47
2	46	Illinois River, ILWW Mile 162.8	40.6684	-89.6110	8/4/2005	14.73	6.19	1.42
2	47	Illinois River, ILWW Mile 160.6	40.6684	-89.6110	8/4/2005	14.59	5.55	1.46
2	48	Illinois River, ILWW Mile 159.4	40.6510	-89.6099	8/4/2005	14.15	5.91	1.57
2	49	Illinois River, ILWW Mile 158.2	40.6393	-89.6183	8/4/2005	14.14	5.07	1.65
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	9/14/2005	8.39	-0.06	3.37
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	9/14/2005	9.94	0.04	3.63
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	9/14/2005	10.77	0.62	3.63
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	9/13/2005	10.94	0.98	3.25
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	9/13/2005	11.22	1.88	3.22
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	9/13/2005	11.20	2.18	2.75
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	9/13/2005	10.62	2.78	2.10
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	10/3/2005	8.02	0.79	3.87
2	2	Chicago Sanitary and Ship Canal, ILWW 290.5	41.5595	-88.0776	10/3/2005	7.98	0.97	4.02
2	3	Des Plaines River, ILWW Mile 287.3	41.5174	-88.0883	10/3/2005	8.4	1.44	4.2
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	10/3/2005	8.63	2.22	3.8
2	5	Des Plaines River, ILWW Mile 285.0	41.4945	-88.1193	10/3/2005	8.9	1.14	3.62
2	6	Des Plaines River, ILWW Mile 282.8	41.4742	-88.1483	10/3/2005	9.32	1.27	3.65
2	7	Des Plaines River, ILWW Mile 280.5	41.4530	-88.1661	10/3/2005	9.57	1.49	3.64
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	10/3/2005	10.02	1.21	4.1
2	9	Des Plaines River, ILWW Mile 276.1	41.4047	-88.2180	10/3/2005	9.43	1.3	4.39
2	10	Des Plaines River, ILWW Mile 274.0	41.3829	-88.2423	10/4/2005	10.04	1.79	4.52
2	11	Illinois River, ILWW Mile 272.4	41.3992	-88.2650	10/4/2005	9.78	1.74	3.87
2	12	Illinois River, ILWW Mile 270.0	41.3920	-88.3103	10/4/2005	9.58	1.78	2.71
2	13	Illinois River, ILWW Mile 276.8	41.3786	-88.3401	10/4/2005	9.52	1.48	2.76
2	14	Illinois River, ILWW Mile 265.0	41.3615	-88.3948	10/4/2005	9.53	0.91	2.89

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N$-NO_3	$\delta^{18}O$-NO_3	NO_3-N (mg/L)
2	15	Illinois River, ILWW Mile 263.0	41.3530	-88.4298	10/4/2005	9.72	1.25	3.13
2	16	Illinois River, ILWW Mile 261.6	41.3476	-88.4562	10/4/2005	9.7	0.96	3.05
2	17	Illinois River, ILWW Mile 256.0	41.3227	-88.5552	10/4/2005	9.85	1.49	3.38
2	18	Illinois River, ILWW Mile 253.0	41.2990	-88.6044	10/4/2005	10.18	1.91	3.14
2	19	Illinois River, ILWW Mile 250.0	41.3139	-88.6549	10/4/2005	9.91	0.7	2.98
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	10/4/2005	9.72	0.59	3.04
2	21	Illinois River, ILWW Mile 246.0	41.3251	-88.7243	10/4/2005	9.44	0.23	3.25
2	22	Illinois River, ILWW Mile 243.7	41.3322	-88.7693	10/4/2005	9.72	0.77	3.17
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	10/4/2005	9.53	0.47	3.25
2	24	Illinois River, ILWW Mile 238.5	41.3362	-88.8642	10/4/2005	9.48	0.34	3.2
2	25	Illinois River, ILWW Mile 236.8	41.3224	-88.8800	10/4/2005	9.77	0.56	3.24
2	26	Illinois River, ILWW Mile 234.5	41.3189	-88.9238	10/4/2005	9.61	0.71	3.34
2	27	Illinois River, ILWW Mile 231.7	41.3215	-88.9771	10/4/2005	9.77	0.61	2.92
2	28	Illinois River, ILWW Mile 229.6	41.3276	-89.0100	10/5/2005	9.91	1.15	2.84
2	29	Illinois River, ILWW Mile 226.9	41.3205	-89.0644	10/5/2005	10.13	1.13	2.8
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	10/5/2005	9.94	0.55	2.99
2	31	Illinois River, ILWW Mile 222.6	41.3233	-89.1241	10/5/2005	10.1	0.85	2.78
2	32	Illinois River, ILWW Mile 219.8	41.3084	-89.1709	10/5/2005	10.14	1	3.06
2	33	Illinois River, ILWW Mile 217.1	41.3136	-89.2253	10/5/2005	10.24	1.1	3.17
2	34	Illinois River, ILWW Mile 213.4	41.3136	-89.2819	10/5/2005	10.32	1.11	3.14
2	35	Illinois River, ILWW Mile 209.4	41.2820	-89.3370	10/5/2005	10.35	1.04	3.31
2	36	Illinois River, ILWW Mile 205.0	41.2220	-89.3588	10/5/2005	10.59	1.24	3.23
2	37	Illinois River, ILWW Mile 200.4	41.1619	-89.3193	10/5/2005	10.67	1.24	3.12
2	38	Illinois River, ILWW Mile 196.9	41.1159	-89.3365	10/5/2005	10.96	0.62	3.06
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	10/5/2005	10.88	1.06	3.14
2	40	Illinois River, ILWW Mile 186.4	40.9878	-89.4385	10/5/2005	11.19	1.38	2.68
2	41	Illinois River, ILWW Mile 183.2	40.9499	-89.4540	10/5/2005	11.39	2.54	2.73
2	42	Illinois River, ILWW Mile 179.0	40.8941	-89.4906	10/5/2005	11.92	2.73	2.4
2	43	Illinois River, ILWW Mile 174.9	40.8410	-89.5242	10/6/2005	11.64	2.61	2.7

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N-NO_3$	$\delta^{18}O-NO_3$	NO_3-N (mg/L)
2	44	Illinois River, ILWW Mile 170.9	40.7127	-89.5475	10/6/2005	12.57	3.59	2.22
2	45	Illinois River, ILWW Mile 165.3	40.6891	-89.5833	10/6/2005	15.26	5.92	1.52
2	46	Illinois River, ILWW Mile 162.8	40.6684	-89.6110	10/6/2005	13.14	3.77	1.87
2	47	Illinois River, ILWW Mile 160.6	40.6684	-89.6110	10/6/2005	13.15	3.86	1.8
2	48	Illinois River, ILWW Mile 159.4	40.6510	-89.6099	10/6/2005	12.6	3.52	2.01
2	49	Illinois River, ILWW Mile 158.2	40.6393	-89.6183	10/6/2005	12.86	3.25	1.97
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	11/2/2005	9.58	-0.44	5.22
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	11/2/2005	9.16	-0.32	6.74
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	11/2/2005	9.90	-0.14	6.55
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	11/1/2005	9.86	0.90	4.65
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	11/1/2005	9.85	1.67	4.63
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	11/1/2005	10.45	1.31	2.87
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	11/1/2005	11.26	3.14	3.55
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	3/30/2006	8.27	2.17	9.21
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	3/30/2006	9.38	2.1	7.77
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	3/30/2006	8.93	2.65	8.17
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	3/29/2006	7.7	3.43	6.27
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	3/29/2006	7.42	3.67	5.87
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	3/29/2006	7.41	3.27	5.86
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	3/29/2006	7.2	4.26	5.74
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	4/20/2006	7.51	3.36	4.01
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	4/20/2006	7.42	3.62	3.26
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	4/20/2006	8.41	4.36	2.99
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	4/19/2006	5.19	3.85	7.75
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	4/19/2006	5.2	4	7.8
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	4/19/2006	4.93	4.21	7.15
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	4/19/2006	6.13	4.24	6.73

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N-NO_3$	$\delta^{18}O-NO_3$	NO_3-N (mg/L)
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	5/1/2006	9.72	2.19	6.4
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	5/1/2006	10.44	2.26	6.06
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	5/1/2006	9.63	2.34	5.6
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	5/2/2006	8.41	3.8	6.48
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	5/2/2006	8.43	4	6.45
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	5/3/2006	7.22	4.04	6.47
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	5/3/2006	7.38	4.39	5.87
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	6/21/2006	9.85	0.94	5.08
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	6/21/2006	11.06	1.73	5.53
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	6/21/2006	10.78	1.61	5.08
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	6/20/2006	9	4.88	5.22
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	6/20/2006	8.97	5.25	5.25
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	6/20/2006	9.36	6.23	5.13
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	6/20/2006	9.18	5.98	4.75
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	7/20/2006	7.28	0.29	4.55
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	7/20/2006	9.37	1.42	5.34
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	7/20/2006	9.27	0.47	4.12
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	7/19/2006	10.46	4.41	4.3
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	7/19/2006	10.29	4.61	4.06
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	7/19/2006	10.92	5.19	3.98
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	7/19/2006	11.28	4.66	3.08
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	8/7/2006	8.11	0.61	4.48
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	8/7/2006	8.3	0.76	5.08
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	8/7/2006	8.71	1.26	3.96
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	8/8/2006	10.38	3.12	3.21
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	8/8/2006	10.41	3.22	3.36

2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	8/9/2006	10.44	2.99	3.02
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	8/9/2006	10.91	2.9	2.61
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	9/21/2006	7.9	-0.53	4.23
Category	**Sample ID**	**Sample Location**	**Latitude (dd.dddd)**	**Longitude (dd.dddd)**	**Sampling Date**	**Nitrogen Data**		
						δ^{15}N-NO_3	**δ^{18}O-NO_3**	**NO_3-N (mg/L)**
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	9/21/2006	8.61	-0.25	3.28
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	9/21/2006	8.71	-0.48	3.56
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	9/20/2006	9.5	3.03	3.53
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	9/20/2006	9.68	2.95	3.39
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	9/20/2006	9.73	3.7	3.01
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	9/20/2006	9.39	4.43	3.09
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5719	-88.0773	10/2/2006	9.76	0.65	5.48
2	4	Des Plaines River, ILWW Mile 286.5	41.5078	-88.0963	10/2/2006	9.75	0.72	5.76
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	10/2/2006	9.8	0.85	5.52
2	20	Illinois River, ILWW Mile 247.5	41.3214	-88.7016	10/3/2006	9.92	2.55	3.99
2	23	Illinois River, ILWW Mile 240.6	41.3388	-88.8238	10/3/2006	9.95	2.16	3.95
2	30	Illinois River, ILWW Mile 224.7	41.3150	-89.0911	10/4/2006	9.9	1.82	4.74
2	39	Illinois River, ILWW Mile 190.0	41.0392	-89.4150	10/4/2006	9.81	2.64	3.49
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5718	-88.0773	3/27/2008	8.65	3.05	4.73
2	4	Des Plaines River, ILWW Mile 286.5	41.5077	-88.0962	3/27/2008	7.36	2.2	4.69
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	3/27/2008	7.21	2.45	4.85
2	20	Illinois River, ILWW Mile 247.5	41.3213	-88.7016	3/26/2008	7.5	3.71	4.99
2	30	Illinois River, ILWW Mile 224.7	41.3153	-89.0910	3/26/2008	7.45	3.28	4.87
2	39	Illinois River, ILWW Mile 190.0	41.0380	-89.4152	3/26/2008	7.19	3.85	5.19
2	45	Illinois River, ILWW Mile 165.3	40.6950	-89.5711	3/26/2008	7.16	4	5.05
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5718	-88.0773	4/24/2008	9.92	2.86	6.77
2	4	Des Plaines River, ILWW Mile 286.5	41.5077	-88.0962	4/24/2008	9.64	2.39	5.21
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	4/24/2008	9.57	1.97	4.26

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data $\delta^{15}N\text{-}NO_3$	Nitrogen Data $\delta^{18}O\text{-}NO_3$	Nitrogen Data $NO_3\text{-}N$ (mg/L)
2	20	Illinois River, ILWW Mile 247.5	41.3213	-88.7016	4/24/2008	8.63	4.18	3.25
2	30	Illinois River, ILWW Mile 224.7	41.3153	-89.0910	4/23/2008	8.69	4.82	2.99
2	39	Illinois River, ILWW Mile 190.0	41.0380	-89.4152	4/23/2008	7.85	4.76	3.8
2	45	Illinois River, ILWW Mile 165.3	40.6950	-89.5711	4/23/2008	7.35	4.43	4.22
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5718	-88.0773	5/22/2008	9.17	1.87	6.36
2	4	Des Plaines River, ILWW Mile 286.5	41.5077	-88.0962	5/22/2008	9.3	1.68	5.82
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	5/22/2008	9.54	1.75	4.58
2	20	Illinois River, ILWW Mile 247.5	41.3213	-88.7016	5/22/2008	8.21	4.37	4.57
2	30	Illinois River, ILWW Mile 224.7	41.3153	-89.0910	5/21/2008	7.52	4.38	4.7
2	39	Illinois River, ILWW Mile 190.0	41.0380	-89.4152	5/21/2008	6.94	4.44	4.98
2	45	Illinois River, ILWW Mile 165.3	40.6950	-89.5711	5/21/2008	7.12	4.99	4.87
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5718	-88.0773	6/19/2008	8.84	1.43	5.06
2	4	Des Plaines River, ILWW Mile 286.5	41.5077	-88.0962	6/19/2008	9.27	1.75	3.73
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	6/19/2008	10.27	2.07	3.92
2	20	Illinois River, ILWW Mile 247.5	41.3213	-88.7016	6/19/2008	8.89	4.23	4.35
2	30	Illinois River, ILWW Mile 224.7	41.3153	-89.0910	6/18/2008	8.33	4.49	3.81
2	39	Illinois River, ILWW Mile 190.0	41.0380	-89.4152	6/18/2008	7.93	4.04	4.19
2	45	Illinois River, ILWW Mile 165.3	40.6950	-89.5711	6/18/2008	8.1	4.47	4.30
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5718	-88.0773	7/17/2008	9.31	1.66	4.65
2	4	Des Plaines River, ILWW Mile 286.5	41.5077	-88.0962	7/17/2008	8.51	0.5	5.17
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	7/17/2008	10.01	0.38	2.15
2	20	Illinois River, ILWW Mile 247.5	41.3213	-88.7016	7/17/2008	11.56	3.68	3.42
2	30	Illinois River, ILWW Mile 224.7	41.3153	-89.0910	7/16/2008	11.88	5.93	3.2
2	39	Illinois River, ILWW Mile 190.0	41.0380	-89.4152	7/16/2008	9.32	5.05	4.79
2	45	Illinois River, ILWW Mile 165.3	40.6950	-89.5711	7/16/2008	9.3	5.83	3.56
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5718	-88.0773	9/11/2008	8.24	-1.12	3.35

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data $\delta^{15}N\text{-}NO_3$	$\delta^{18}O\text{-}NO_3$	$NO_3\text{-}N$ (mg/L)
2	4	Des Plaines River, ILWW Mile 286.5	41.5077	-88.0962	9/11/2008	7.76	-1.17	3.11
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	9/11/2008	8.41	-0.09	3.2
2	20	Illinois River, ILWW Mile 247.5	41.3213	-88.7016	9/11/2008	8.67	0.15	2.87
2	30	Illinois River, ILWW Mile 224.7	41.3153	-89.0910	9/10/2008	9.3	1.74	2.57
2	39	Illinois River, ILWW Mile 190.0	41.0380	-89.4152	9/10/2008	9.84	1.96	2.93
2	45	Illinois River, ILWW Mile 165.3	40.6950	-89.5711	9/10/2008	10.56	1.9	3.19
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5718	-88.0773	10/2/2008	8.43	-0.55	3.23
2	4	Des Plaines River, ILWW Mile 286.5	41.5077	-88.0962	10/2/2008	8.08	-0.3	3.25
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	10/2/2008	8.78	-0.5	3.11
2	20	Illinois River, ILWW Mile 247.5	41.3213	-88.7016	10/2/2008	9.52	0.88	2.16
2	30	Illinois River, ILWW Mile 224.7	41.3153	-89.0910	10/1/2008	9.99	2.91	2.32
2	39	Illinois River, ILWW Mile 190.0	41.0380	-89.4152	10/1/2008	9.77	3.24	2.16
2	45	Illinois River, ILWW Mile 165.3	40.6950	-89.5711	10/1/2008	9.36	3.93	1.99
2	1	Chicago Sanitary and Ship Canal, ILWW 291.5	41.5718	-88.0773	10/23/2008	8.68	-0.29	6.28
2	4	Des Plaines River, ILWW Mile 286.5	41.5077	-88.0962	10/23/2008	9.4	-0.39	5.95
2	8	Des Plaines River, ILWW Mile 278.0	41.4216	-88.1938	10/23/2008	9.76	0.65	6.74
2	20	Illinois River, ILWW Mile 247.5	41.3213	-88.7016	10/23/2008	10.47	2.93	3.68
2	30	Illinois River, ILWW Mile 224.7	41.3153	-89.0910	10/22/2008	10.72	4.01	3.79
2	39	Illinois River, ILWW Mile 190.0	41.0380	-89.4152	10/22/2008	10.07	3.92	3.64
2	45	Illinois River, ILWW Mile 165.3	40.6950	-89.5711	10/22/2008	10.6	4.4	2.85
3	DP	Des Plaines River	41.5965	-88.0687	3/27/2008	9.35	5.24	2.65
3	DR	DuPage River	41.4208	-88.2274	3/27/2008	9.45	4.11	4.06
3	DP	Des Plaines River	41.5965	-88.0687	4/24/2008	11.65	3.32	2.34
3	DR	DuPage River	41.4208	-88.2274	4/24/2008	10.62	3.42	4.47
3	DP	Des Plaines River	41.5965	-88.0687	5/22/2008	12.97	4.67	2.76
3	DR	DuPage River	41.4208	-88.2274	5/22/2008	10.41	2.82	4.42
3	DP	Des Plaines River	41.5965	-88.0687	6/19/2008	11.67	4.2	2.04

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						$\delta^{15}N\text{-}NO_3$	$\delta^{18}O\text{-}NO_3$	NO_3-N (mg/L)
3	DR	DuPage River	41.4208	-88.2274	6/19/2008	10.66	2.82	3.42
3	DP	Des Plaines River	41.5965	-88.0687	7/17/2008	11.2	1.8	4.5
3	DR	DuPage River	41.4208	-88.2274	7/17/2008	11.71	3.1	3.57
3	DP	Des Plaines River	41.5965	-88.0687	9/11/2008	9.79	0.8	2.32
3	DR	DuPage River	41.4208	-88.2274	9/11/2008	9.86	0.92	2.35
3	DP	Des Plaines River	41.5965	-88.0687	10/2/2008	10.07	2.14	3.41
3	DR	DuPage River	41.4208	-88.2274	10/2/2008	10.82	2.3	4.81
3	DP	Des Plaines River	41.5965	-88.0687	10/23/2008	11.31	1.78	6.45
3	DR	DuPage River	41.4208	-88.2274	10/23/2008	10.26	2.2	7.15
4	KR	Kankakee River	41.3671	-88.2485	3/27/2008	7.47	4.85	4.14
4	FR	Fox River	41.3461	-88.8398	3/26/2008	8.59	4.43	2.67
4	KR	Kankakee River	41.3671	-88.2485	4/24/2008	8.31	5.01	2.6
4	FR	Fox River	41.3461	-88.8398	4/23/2008	9.37	4.92	1.94
4	KR	Kankakee River	41.3671	-88.2485	5/22/2008	6.95	4.45	4.01
4	FR	Fox River	41.3461	-88.8398	5/21/2008	8.14	5.29	3.32
4	KR	Kankakee River	41.3671	-88.2485	6/19/2008	8.25	4.94	4.21
4	FR	Fox River	41.3461	-88.8398	6/18/2008	9.43	4.81	1.86
4	KR	Kankakee River	41.3671	-88.2485	7/17/2008	10.69	6.83	3.04
4	FR	Fox River	41.3461	-88.8398	7/16/2008	11.24	8.42	1.18
4	KR	Kankakee River	41.3671	-88.2485	9/11/2008	10.5	2.98	0.93
4	FR	Fox River	41.3461	-88.8398	9/10/2008	11.33	4.29	1.39
4	KR	Kankakee River	41.3671	-88.2485	10/2/2008	10.75	4.32	1.04
4	FR	Fox River	41.3461	-88.8398	10/1/2008	11.22	5.46	2.16
4	KR	Kankakee River	41.3671	-88.2485	10/23/2008	10.85	5.53	2.06
4	FR	Fox River	41.3461	-88.8398	10/22/2008	11.31	4.89	2.44
5	AC	Aux Sable Creek	41.3959	-88.3302	3/27/2008	8.97	6.52	7.11
5	MR	Mazon River	41.3515	-88.4200	3/27/2008	8.12	5.94	7.06
5	VR	Vermilion River	41.3173	-89.0676	3/26/2008	6.05	5.13	9.26
5	BC	Bureau Creek	41.2792	-89.3833	3/26/2008	5.89	4.86	9.71

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data		
						δ^{15}N-NO_3	δ^{18}O-NO_3	NO_3-N (mg/L)
5	SL	Senachwine Lake	41.1442	-89.3386	3/26/2008	6.98	4.65	5.07
5	AC	Aux Sable Creek	41.3959	-88.3302	4/24/2008	9.27	6.34	6.28
5	MR	Mazon River	41.3515	-88.4200	4/24/2008	8.36	6.43	6.81
5	VR	Vermilion River	41.3173	-89.0676	4/23/2008	6.84	6.27	8.27
5	BC	Bureau Creek	41.2792	-89.3833	4/23/2008	5.58	5.02	10.54
5	SL	Senachwine Lake	41.1442	-89.3386	4/23/2008	6.94	5.3	5.26
5	AC	Aux Sable Creek	41.3959	-88.3302	5/22/2008	6.69	4.99	9.93
5	MR	Mazon River	41.3515	-88.4200	5/22/2008	6.59	5.5	8.81
5	VR	Vermilion River	41.3173	-89.0676	5/21/2008	6.51	5.37	9.09
5	BC	Bureau Creek	41.2792	-89.3833	5/21/2008	4.75	3.98	11.09
5	SL	Senachwine Lake	41.1442	-89.3386	5/21/2008	6.97	6.02	6.9
5	AC	Aux Sable Creek	41.3959	-88.3302	6/19/2008	8.69	5.97	11.91
5	MR	Mazon River	41.3515	-88.4200	6/19/2008	10	7.6	8.13
5	VR	Vermilion River	41.3173	-89.0676	6/18/2008	6.65	5.67	11.76
5	BC	Bureau Creek	41.2792	-89.3833	6/18/2008	4.25	3.35	15.88
5	SL	Senachwine Lake	41.1442	-89.3386	6/18/2008	6.7	4.82	6.83
5	AC	Aux Sable Creek	41.3959	-88.3302	7/17/2008	12.69	3.81	2.41
5	MR	Mazon River	41.3515	-88.4200	7/17/2008	14.17	9.01	4.51
5	VR	Vermilion River	41.3173	-89.0676	7/16/2008	9.4	7.42	7.18
5	BC	Bureau Creek	41.2792	-89.3833	7/16/2008	4.97	4.55	13.04
5	SL	Senachwine Lake	41.1442	-89.3386	7/16/2008	5.47	4.94	7.26
5	AC	Aux Sable Creek	41.3959	-88.3302	9/11/2008	10.93	6.81	0.7
5	MR	Mazon River	41.3515	-88.4200	9/11/2008	10.62	3.37	1.27
5	VR	Vermilion River	41.3173	-89.0676	9/10/2008	11.67	5.51	1.14
5	BC	Bureau Creek	41.2792	-89.3833	9/10/2008	11.43	7.77	2.2
5	SL	Senachwine Lake	41.1442	-89.3386	9/10/2008	15.56	14.76	0.02
5	AC	Aux Sable Creek	41.3959	-88.3302	10/2/2008	13.52	9.35	3.56
5	MR	Mazon River	41.3515	-88.4200	10/2/2008	12.46	8.63	3.75
5	VR	Vermilion River	41.3173	-89.0676	10/1/2008	10.66	8.43	5.02

Category	Sample ID	Sample Location	Latitude (dd.dddd)	Longitude (dd.dddd)	Sampling Date	Nitrogen Data $\delta^{15}N$-NO_3	$\delta^{18}O$-NO_3	NO_3-N (mg/L)
5	BC	Bureau Creek	41.2792	-89.3833	10/1/2008	6.99	6.46	9.12
5	SL	Senachwine Lake	41.1442	-89.3386	10/1/2008	8.83	4.7	2.55
5	AC	Aux Sable Creek	41.3959	-88.3302	10/23/2008	14.86	10.48	3.9
5	MR	Mazon River	41.3515	-88.4200	10/23/2008	14.43	9.46	3.69
5	VR	Vermilion River	41.3173	-89.0676	10/22/2008	11.03	8.46	6.31
5	BC	Bureau Creek	41.2792	-89.3833	10/22/2008	8.06	7.38	6.95
5	SL	Senachwine Lake	41.1442	-89.3386	10/22/2008	10.96	7.25	2.3
6	FHW	Farmhouse well	41.2377	-89.3309	7/29/2004	4.86	4.15	3.85
6	FHW	Farmhouse well	41.2377	-89.3309	5/19/2005	4.85	4.10	3.50
6	FHW	Farmhouse well	41.2377	-89.3309	8/3/2005	4.60	3.56	3.89
6	LDW	Lake dock well	41.2096	-89.3231	7/29/2004	4.42	3.62	3.30
6	LDW	Lake dock well	41.2096	-89.3231	5/19/2005	4.18	2.94	2.38

Table 5 Anion data, δ^2H-H_2O values, and $\delta^{18}O$-H_2O values of sampling program 1

Sample ID	Sample Location (Sampling program 1)	Sampling Date	Cl^- (mg/L)	SO_4^{2-} (mg/L)	δ^2H of H_2O (‰)	$\delta^{18}O$ of H_2O (‰)
SWRP	Stickney Wastewater Reclamation Plant	10/19/2004	121	86.8	-43.90	-5.81
1	Chicago Sanitary and Ship Canal, ILWW 291.5	10/15/2004	102.4	83	-41.90	-5.53
2	Chicago Sanitary and Ship Canal, ILWW 290.5	10/15/2004	106.3	85.3	-40.80	-5.62
3	Des Plaines River, ILWW Mile 287.3	10/15/2004	108.5	87.5	-40.80	-5.42
4	Des Plaines River, ILWW Mile 286.5	10/15/2004	108.4	83.4	-40.20	-5.39
5	Des Plaines River, ILWW Mile 285.0	10/15/2004	113.6	80.2	-39.70	-5.32
6	Des Plaines River, ILWW Mile 282.8	10/15/2004	113.2	78.2	-38.70	-5.18
7	Des Plaines River, ILWW Mile 280.5	10/15/2004	117.2	84.3	-40.30	-5.40
8	Des Plaines River, ILWW Mile 278.0	10/15/2004	125.3	91.2	-41.10	-5.46
9	Des Plaines River, ILWW Mile 276.1	10/15/2004	123.1	90.5	-41.50	-5.52
10	Des Plaines River, ILWW Mile 274.0	10/14/2004	127	91.1	-40.10	-5.41
11	Illinois River, ILWW Mile 272.4	10/14/2004	119.2	96.7	-41.40	-5.64
12	Illinois River, ILWW Mile 270.0	10/14/2004	89.9	101	-42.70	-5.98
13	Illinois River, ILWW Mile 276.8	10/14/2004	86.9	102.8	-41.60	-6.01
14	Illinois River, ILWW Mile 265.0	10/14/2004	87.1	104.5	-43.60	-6.09
15	Illinois River, ILWW Mile 263.0	10/14/2004	90.4	100.7	-41.50	-5.97
16	Illinois River, ILWW Mile 261.6	10/14/2004	90	99.8	-42.60	-5.96
17	Illinois River, ILWW Mile 256.0	10/14/2004	79.3	86	-41.30	-5.76
18	Illinois River, ILWW Mile 253.0	10/14/2004	88.5	99.9	-42.50	-5.90
19	Illinois River, ILWW Mile 250.0	10/14/2004	92.4	97.6	-42.90	-5.85
20	Illinois River, ILWW Mile 247.5	10/14/2004	101.9	98.8	-41.20	-5.50
21	Illinois River, ILWW Mile 246.0	10/14/2004	88.1	89	-41.10	-5.67
22	Illinois River, ILWW Mile 243.7	10/14/2004	88.6	92.6	-41.80	-5.65

Sample ID	Sample Location (Sampling program 1)	Sampling Date	Cl^- (mg/L)	SO_4^{2-} (mg/L)	δ^2H of H_2O (‰)	$\delta^{18}O$ of H_2O (‰)
23	Illinois River, ILWW Mile 240.6	10/14/2004	89.4	93.1	-41.00	-5.65
24	Illinois River, ILWW Mile 238.5	10/14/2004	100	86.6	-40.10	-5.60
25	Illinois River, ILWW Mile 236.8	10/14/2004	95.6	92.6	-38.70	-5.58
26	Illinois River, ILWW Mile 234.5	10/14/2004	96.3	96.2	-40.10	-5.64
27	Illinois River, ILWW Mile 231.7	10/13/2004	102.9	90.8	-39.50	-5.53
28	Illinois River, ILWW Mile 229.6	10/13/2004	105.7	88.5	-40.30	-5.41
29	Illinois River, ILWW Mile 226.9	10/13/2004	106.2	91.1	-39.60	-5.39
30	Illinois River, ILWW Mile 224.7	10/13/2004	104.6	91.7	-39.50	-5.50
31	Illinois River, ILWW Mile 222.6	10/13/2004	104.2	93.4	-41.90	-5.54
32	Illinois River, ILWW Mile 219.8	10/13/2004	104	93.2	-40.30	-5.53
33	Illinois River, ILWW Mile 217.1	10/13/2004	104.6	94.1	-39.50	-5.46
34	Illinois River, ILWW Mile 213.4	10/13/2004	102.7	94.1	-39.80	-5.55
35	Illinois River, ILWW Mile 209.4	10/13/2004	105.3	91.5	-41.00	-5.53
36	Illinois River, ILWW Mile 205.0	10/13/2004	101.9	94.9	-39.70	-5.48
37	Illinois River, ILWW Mile 200.4	10/13/2004	101.8	96	-40.60	-5.52
38	Illinois River, ILWW Mile 196.9	10/13/2004	99.1	95.6	-39.30	-5.42
39	Illinois River, ILWW Mile 190.0	10/13/2004	100.7	92.6	-39.30	-5.30
40	Illinois River, ILWW Mile 186.4	10/13/2004	100.2	93.7	-37.90	-5.39
41	Illinois River, ILWW Mile 183.2	10/13/2004	91.6	86.4	-37.90	-5.41
42	Illinois River, ILWW Mile 179.0	10/13/2004	92.1	86.8	-38.70	-5.20
43	Illinois River, ILWW Mile 174.9	10/12/2004	88.7	92.7	-37.30	-5.26
44	Illinois River, ILWW Mile 170.9	10/12/2004	85.2	93.4	-38.00	-5.27
45	Illinois River, ILWW Mile 165.3	10/12/2004	78.6	79.2	-36.70	-5.07
46	Illinois River, ILWW Mile 162.8	10/12/2004	82.6	87	-37.30	-5.16
47	Illinois River, ILWW Mile 160.6	10/12/2004	84.8	89.8	-37.40	-5.15
48	Illinois River, ILWW Mile 159.4	10/12/2004	85	86.5	-38.40	-5.11

49	Illinois River, ILWW Mile 158.2	10/12/2004	87.4	90	-37.00	-5.15
Sample ID	**Sample Location (Sampling program 1)**	**Sampling Date**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**	**δ^2H of H_2O (‰)**	**$\delta^{18}O$ of H_2O (‰)**
SWRP	Stickney Wastewater Reclamation Plant	4/29/2005	205.6	106.6	-42.18	-6.30
1	Chicago Sanitary and Ship Canal, ILWW 291.5	5/2/2005	202.1	107.6	-45.88	-6.50
2	Chicago Sanitary and Ship Canal, ILWW 290.5	5/2/2005	203	108	-47.63	-6.44
3	Des Plaines River, ILWW Mile 287.3	5/2/2005	227.8	110.9	-46.82	-6.56
4	Des Plaines River, ILWW Mile 286.5	5/2/2005	226.9	112.4	-46.14	-6.55
5	Des Plaines River, ILWW Mile 285.0	5/2/2005	229.8	118.7	-47.48	-6.52
6	Des Plaines River, ILWW Mile 282.8	5/2/2005	231	115.7	-47.30	-6.53
7	Des Plaines River, ILWW Mile 280.5	5/2/2005	231.1	115.2	-47.97	-6.57
8	Des Plaines River, ILWW Mile 278.0	5/2/2005	229.9	116.1	-47.61	-6.57
9	Des Plaines River, ILWW Mile 276.1	5/2/2005	231.5	116.1	-46.32	-6.64
10	Des Plaines River, ILWW Mile 274.0	5/3/2005	233.2	116.7	-47.15	-6.59
11	Illinois River, ILWW Mile 272.4	5/3/2005	161.2	110.9	-47.01	-6.82
12	Illinois River, ILWW Mile 270.0	5/3/2005	114.6	109.5	-48.07	-6.70
13	Illinois River, ILWW Mile 276.8	5/3/2005	109.9	109.7	-46.95	-6.94
14	Illinois River, ILWW Mile 265.0	5/3/2005	130.2	111.9	-44.75	-6.88
15	Illinois River, ILWW Mile 263.0	5/3/2005	121.8	110	-46.05	-6.81
16	Illinois River, ILWW Mile 261.6	5/3/2005	129	110.9	-43.82	-6.79
17	Illinois River, ILWW Mile 256.0	5/3/2005	123.9	104.8	-43.68	-6.91
18	Illinois River, ILWW Mile 253.0	5/3/2005	116.2	104	-39.71	-6.81
19	Illinois River, ILWW Mile 250.0	5/3/2005	120.3	103.2	-40.93	-6.82
20	Illinois River, ILWW Mile 247.5	5/3/2005	121.5	103.4	-42.48	-6.90
21	Illinois River, ILWW Mile 246.0	5/3/2005	100.7	99.9	-41.08	-6.77
22	Illinois River, ILWW Mile 243.7	5/3/2005	115.2	101.8	-40.54	-6.82
23	Illinois River, ILWW Mile 240.6	5/3/2005	103.7	100.3	-41.01	-6.89

Sample ID	Sample Location (Sampling program 1)	Sampling Date	Cl^- (mg/L)	SO_4^{2-} (mg/L)	δ^2H of H_2O (‰)	$\delta^{18}O$ of H_2O (‰)
24	Illinois River, ILWW Mile 238.5	5/3/2005	108.2	92.4	-37.16	-6.86
25	Illinois River, ILWW Mile 236.8	5/3/2005	108.4	94.9	-41.78	-6.81
26	Illinois River, ILWW Mile 234.5	5/3/2005	116.2	95.7	-42.69	-6.84
27	Illinois River, ILWW Mile 231.7	5/4/2005	109.5	95.2	-44.96	-6.88
28	Illinois River, ILWW Mile 229.6	5/4/2005	111.1	92.3	-46.21	-6.83
29	Illinois River, ILWW Mile 226.9	5/4/2005	113	93.1	-45.29	-6.78
30	Illinois River, ILWW Mile 224.7	5/4/2005	112.4	92	-45.99	-6.54
31	Illinois River, ILWW Mile 222.6	5/4/2005	106	88.3	-46.63	-6.75
32	Illinois River, ILWW Mile 219.8	5/4/2005	108.8	88.4	-45.01	-6.62
33	Illinois River, ILWW Mile 217.1	5/4/2005	104.6	83.5	-41.74	-6.67
34	Illinois River, ILWW Mile 213.4	5/4/2005	111.2	88.7	-41.62	-6.77
35	Illinois River, ILWW Mile 209.4	5/4/2005	111.1	89.1	-41.16	-6.71
36	Illinois River, ILWW Mile 205.0	5/4/2005	109.7	88.4	-43.20	-6.68
37	Illinois River, ILWW Mile 200.4	5/4/2005	105	87.5	-41.57	-6.79
38	Illinois River, ILWW Mile 196.9	5/4/2005	100.5	85.7	-40.49	-6.60
39	Illinois River, ILWW Mile 190.0	5/4/2005	99.3	85.7	-44.77	-6.67
40	Illinois River, ILWW Mile 186.4	5/4/2005	98.5	84.3	-40.53	-6.66
41	Illinois River, ILWW Mile 183.2	5/4/2005	93.5	80.3	-41.43	-6.47
42	Illinois River, ILWW Mile 179.0	5/4/2005	92.2	80.2	-39.82	-6.58
43	Illinois River, ILWW Mile 174.9	5/5/2005	93.8	80.6	-40.63	-6.59
44	Illinois River, ILWW Mile 170.9	5/5/2005	93.8	80.5	-41.09	-6.36
45	Illinois River, ILWW Mile 165.3	5/5/2005	95.1	80.1	-42.35	-6.50
46	Illinois River, ILWW Mile 162.8	5/5/2005	95.8	80.3	-39.61	-6.46
47	Illinois River, ILWW Mile 160.6	5/5/2005	96.7	80.3	-39.75	-6.48
48	Illinois River, ILWW Mile 159.4	5/5/2005	97.4	80.8	-40.11	-6.41
49	Illinois River, ILWW Mile 158.2	5/5/2005	97.6	82.5	-40.52	-6.20

Sample ID	Sample Location (Sampling program 1)	Sampling Date	Cl^- (mg/L)	SO_4^{2-} (mg/L)	δ^2H of H_2O (‰)	$\delta^{18}O$ of H_2O (‰)
SWRP	Stickney Wastewater Reclamation Plant	8/1/2005	105.2	58.3	-46.07	-6.10
1	Chicago Sanitary and Ship Canal, ILWW 291.5	8/1/2005	98	62	-41.35	-5.70
2	Chicago Sanitary and Ship Canal, ILWW 290.5	8/1/2005	100	62.6	-41.66	-5.81
3	Des Plaines River, ILWW Mile 287.3	8/1/2005	106.8	63.4	-40.04	-5.68
4	Des Plaines River, ILWW Mile 286.5	8/1/2005	106.7	62.4	-41.97	-5.67
5	Des Plaines River, ILWW Mile 285.0	8/1/2005	109.4	69.6	-41.17	-5.60
6	Des Plaines River, ILWW Mile 282.8	8/1/2005	109.7	69.4	-41.29	-5.28
7	Des Plaines River, ILWW Mile 280.5	8/1/2005	118.4	80.4	-42.41	-5.35
8	Des Plaines River, ILWW Mile 278.0	8/1/2005	109.2	78.3	-40.36	-5.44
9	Des Plaines River, ILWW Mile 276.1	8/1/2005	114.2	78.5	-38.75	-5.37
10	Des Plaines River, ILWW Mile 274.0	8/2/2005	113.7	79.6	-39.36	-5.23
11	Illinois River, ILWW Mile 272.4	8/2/2005	87.1	91.6	-37.97	-5.03
12	Illinois River, ILWW Mile 270.0	8/2/2005	88.7	85.7	-38.00	-5.03
13	Illinois River, ILWW Mile 276.8	8/2/2005	89.7	87	-38.56	-5.08
14	Illinois River, ILWW Mile 265.0	8/2/2005	93.6	83.3	-38.50	-5.20
15	Illinois River, ILWW Mile 263.0	8/2/2005	93	84.2	-32.69	-5.20
16	Illinois River, ILWW Mile 261.6	8/2/2005	93.7	85.1	-37.44	-5.19
17	Illinois River, ILWW Mile 256.0	8/2/2005	96.3	86.5	-37.88	-5.18
18	Illinois River, ILWW Mile 253.0	8/2/2005	97.1	88	-39.85	-5.13
19	Illinois River, ILWW Mile 250.0	8/2/2005	97.2	89.7	-33.55	-5.26
20	Illinois River, ILWW Mile 247.5	8/2/2005	100	92.6	-36.81	-5.12
21	Illinois River, ILWW Mile 246.0	8/2/2005	98.8	91.4	-36.93	-5.15
22	Illinois River, ILWW Mile 243.7	8/2/2005	99.7	92.7	-37.70	-5.08
23	Illinois River, ILWW Mile 240.6	8/2/2005	99	92.4	-38.01	-5.03

Sample ID	Sample Location (Sampling program 1)	Sampling Date	Cl^- (mg/L)	SO_4^{2-} (mg/L)	δ^2H of H_2O (‰)	$\delta^{18}O$ of H_2O (‰)
24	Illinois River, ILWW Mile 238.5	8/2/2005	114.7	84.7	-40.66	-5.09
25	Illinois River, ILWW Mile 236.8	8/2/2005	112.8	86	-40.53	-5.12
26	Illinois River, ILWW Mile 234.5	8/2/2005	101.8	91.4	-41.86	-5.05
27	Illinois River, ILWW Mile 231.7	8/3/2005	106	88.3	-40.96	-5.06
28	Illinois River, ILWW Mile 229.6	8/3/2005	102.8	89.7	-41.47	-5.08
29	Illinois River, ILWW Mile 226.9	8/3/2005	105.9	91.8	-39.66	-5.10
30	Illinois River, ILWW Mile 224.7	8/3/2005	105.2	89.3	-38.88	-5.08
31	Illinois River, ILWW Mile 222.6	8/3/2005	106.7	88	-41.12	-5.15
32	Illinois River, ILWW Mile 219.8	8/3/2005	106.7	87.8	-31.96	-5.11
33	Illinois River, ILWW Mile 217.1	8/3/2005	106	88.2	-41.38	-5.16
34	Illinois River, ILWW Mile 213.4	8/3/2005	106.3	88	-41.16	-5.05
35	Illinois River, ILWW Mile 209.4	8/3/2005	104.4	89.2	-39.94	-4.95
36	Illinois River, ILWW Mile 205.0	8/3/2005	106.9	88.6	-40.43	-5.00
37	Illinois River, ILWW Mile 200.4	8/3/2005	107.2	83.9	-40.02	-4.92
38	Illinois River, ILWW Mile 196.9	8/3/2005	107.9	85.5	-39.29	-5.03
39	Illinois River, ILWW Mile 190.0	8/3/2005	111.5	91	-38.33	-4.89
40	Illinois River, ILWW Mile 186.4	8/3/2005	109.1	88.8	-41.12	-4.78
41	Illinois River, ILWW Mile 183.2	8/3/2005	107.6	89.1	-39.03	-4.85
42	Illinois River, ILWW Mile 179.0	8/3/2005	104.9	88.9	-37.41	-4.55
43	Illinois River, ILWW Mile 174.9	8/4/2005	109.4	89.7	-38.12	-4.59
44	Illinois River, ILWW Mile 170.9	8/4/2005	112.4	88.4	-32.75	-4.28
45	Illinois River, ILWW Mile 165.3	8/4/2005	112.3	87.4	-35.51	-4.34
46	Illinois River, ILWW Mile 162.8	8/4/2005	115.2	87.8	-37.25	-4.27
47	Illinois River, ILWW Mile 160.6	8/4/2005	116.2	88.8	-37.03	-4.31
48	Illinois River, ILWW Mile 159.4	8/4/2005	119.3	89.4	-37.60	-4.34
49	Illinois River, ILWW Mile 158.2	8/4/2005	118.6	89.2	-35.33	-4.36

Sample ID	Sample Location (Sampling program 1)	Sampling Date	Cl^- (mg/L)	SO_4^{2-} (mg/L)	δ^2H of H_2O (‰)	$\delta^{18}O$ of H_2O (‰)
SWRP	Stickney Wastewater Reclamation Plant	10/3/2005	93.3	61.9	-32.82	-5.28
1	Chicago Sanitary and Ship Canal, ILWW 291.5	10/3/2005	64.2	47.2	-39.15	-5.48
2	Chicago Sanitary and Ship Canal, ILWW 290.5	10/3/2005	67.1	48.9	-39.76	-5.44
3	Des Plaines River, ILWW Mile 287.3	10/3/2005	80.1	51.8	-38.23	-5.34
4	Des Plaines River, ILWW Mile 286.5	10/3/2005	72.6	49.6	-38.87	-5.30
5	Des Plaines River, ILWW Mile 285.0	10/3/2005	73.7	55.2	-39.04	-5.68
6	Des Plaines River, ILWW Mile 282.8	10/3/2005	74.9	55.9	-38.49	-5.40
7	Des Plaines River, ILWW Mile 280.5	10/3/2005	78.6	56.4	-36.12	-5.23
8	Des Plaines River, ILWW Mile 278.0	10/3/2005	83.7	60.5	-38.39	-5.28
9	Des Plaines River, ILWW Mile 276.1	10/3/2005	90.3	63	-38.48	-5.36
10	Des Plaines River, ILWW Mile 274.0	10/4/2005	92.6	63.7	-38.23	-5.30
11	Illinois River, ILWW Mile 272.4	10/4/2005	85.2	70.1	-38.88	-5.38
12	Illinois River, ILWW Mile 270.0	10/4/2005	70.5	84.6	-36.29	-5.52
13	Illinois River, ILWW Mile 276.8	10/4/2005	70.7	85	-39.26	-5.54
14	Illinois River, ILWW Mile 265.0	10/4/2005	72.7	82.8	-39.42	-5.59
15	Illinois River, ILWW Mile 263.0	10/4/2005	75.4	79.1	-40.62	-5.53
16	Illinois River, ILWW Mile 261.6	10/4/2005	74.6	80.5	-39.97	-5.62
17	Illinois River, ILWW Mile 256.0	10/4/2005	81.4	75.8	-39.85	-5.50
18	Illinois River, ILWW Mile 253.0	10/4/2005	79.4	81.2	-40.44	-5.56
19	Illinois River, ILWW Mile 250.0	10/4/2005	75.2	82.3	-39.58	-5.73
20	Illinois River, ILWW Mile 247.5	10/4/2005	79	86.1	-40.76	-5.38
21	Illinois River, ILWW Mile 246.0	10/4/2005	84.5	99.9	-39.11	-5.30
22	Illinois River, ILWW Mile 243.7	10/4/2005	81.9	93.2	-39.12	-5.37
23	Illinois River, ILWW Mile 240.6	10/4/2005	85.4	99.7	-38.32	-5.26
24	Illinois River, ILWW Mile 238.5	10/4/2005	89	87.1	-38.89	-5.27
25	Illinois River, ILWW Mile 236.8	10/4/2005	88.9	84.6	-34.60	-5.27
26	Illinois River, ILWW Mile 234.5	10/4/2005	112.5	91.7	-38.84	-5.12

27	Illinois River, ILWW Mile 231.7	10/4/2005	90.7	86.3	-38.09	-5.32
Sample ID	**Sample Location (Sampling program 1)**	**Sampling Date**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**	**δ^2H of H_2O (‰)**	**$\delta^{18}O$ of H_2O (‰)**
28	Illinois River, ILWW Mile 229.6	10/5/2005	92.5	80.3	-36.29	-5.06
29	Illinois River, ILWW Mile 226.9	10/5/2005	93.8	75.9	-32.44	-4.96
30	Illinois River, ILWW Mile 224.7	10/5/2005	98.6	82.8	-34.72	-5.01
31	Illinois River, ILWW Mile 222.6	10/5/2005	86.2	70.5	-35.96	-4.92
32	Illinois River, ILWW Mile 219.8	10/5/2005	92.2	78	-33.09	-5.03
33	Illinois River, ILWW Mile 217.1	10/5/2005	93.7	76.9	-34.36	-4.91
34	Illinois River, ILWW Mile 213.4	10/5/2005	95.3	73.1	-31.48	-4.94
35	Illinois River, ILWW Mile 209.4	10/5/2005	102.6	79.3	-33.49	-4.94
36	Illinois River, ILWW Mile 205.0	10/5/2005	99.3	72.1	-36.08	-4.88
37	Illinois River, ILWW Mile 200.4	10/5/2005	95.2	71.2	-33.20	-5.17
38	Illinois River, ILWW Mile 196.9	10/5/2005	95.7	73.5	-34.03	-4.89
39	Illinois River, ILWW Mile 190.0	10/5/2005	96.9	76.2	-34.21	-5.09
40	Illinois River, ILWW Mile 186.4	10/5/2005	94.1	77.4	-33.79	-4.97
41	Illinois River, ILWW Mile 183.2	10/5/2005	93.5	78.5	-34.04	-5.23
42	Illinois River, ILWW Mile 179.0	10/5/2005	92.7	81.1	-33.72	-5.05
43	Illinois River, ILWW Mile 174.9	10/6/2005	94.2	80.5	-33.97	-5.04
44	Illinois River, ILWW Mile 170.9	10/6/2005	91.7	81.4	-31.75	-4.91
45	Illinois River, ILWW Mile 165.3	10/6/2005	90.8	81.7	-31.78	-4.80
46	Illinois River, ILWW Mile 162.8	10/6/2005	92.2	81.5	-32.25	-4.81
47	Illinois River, ILWW Mile 160.6	10/6/2005	91	79	-31.90	-4.88
48	Illinois River, ILWW Mile 159.4	10/6/2005	89.1	78.5	-30.68	-4.81
49	Illinois River, ILWW Mile 158.2	10/6/2005	91.9	80.4	-32.67	-4.90

VITA

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Education

2002-2006 **B.S., Applied Chemistry**

Nanjing Normal University, China

2006-2009 **M.S., Geochemistry and Quaternary Geology**

Nanjing Normal University, China

Advisor: Dr. Hao Yang

Thesis: "The study of temporal evolution of heavy metal and nutrients in modern lake sediments of Fuxianhu Lake."

2009-2015 **Ph.D., Earth and Environmental Sciences**

University of Illinois at Chicago

Advisor: Dr. Neil Sturchio

Dissertation: "Seasonal variations in nitrate flux, transport, and sources in the Upper Illinois River Basin."

University Teaching Experience

Undergraduate Level

Department of Earth and Environmental Sciences, University of Illinois at Chicago

Global Environmental Change (EaES 101)

(2009 Fall, 2010 Spring, 2010 Fall, 2011 Spring, 2012 Fall)

Earth, Energy, and the Environment (EaES111)

(2013 Fall, 2014 Spring)

Field Work in Missouri (spring break field trip)

(2012 Spring Break)

Graduate Level

Department of Earth and Environmental Sciences, University of Illinois at Chicago

Hydrology/Hydrogeology (EaES 475) (2011 Fall, 2014 Fall)

Environmental Geochemistry (EaES 415) (2013 Spring)

Research Experience

Master projects at Nanjing Normal University (2006-2009)

- Measurement and modeling of the sedimentation rate and study on the temporal and spatial distribution of nutrients and heavy metals in the Fuxianhu Lake Watershed, China
- Isotopic study (^{137}Cs, ^{210}Pb) of variations in soil erosion rates under different land use in Southwestern China

Research Assistant at University of Illinois at Chicago (2009-2015)

- Geochemical study of riverine nitrate: applying measurements of nitrate concentration and isotopes (^{15}N, ^{18}O) to study the sources and in-stream processes of nitrate
- Hydrological modeling on the watershed scale (the Upper Illinois River Basin) of the source mixing and in-stream processes (denitrification) of nitrate, and human impact on basin nutrient export
- Analyze the spatial and temporal distribution of riverine nitrate and land use patterns in the Upper Illinois River basin with ArcGIS tools
- Isotopic study (^{226}Ra, ^{228}Ra) on Egyptian groundwater. Developed laboratory methods for effective Ra adsorption on Mn oxide-coated stainless steel discs and measurement by isotope-dilution alpha spectrometry using a ^{224}Ra spike.
- Application of strontium isotopes ($^{87}Sr/^{86}Sr$) and major ions in groundwater to distinguish major sources of solutes and flow paths in Northern Illinois. Participated in the sampling and measurement of Sr isotope ratios in river water using Sr-Spec resin and Thermal Ionization Mass Spectrometry.

Conference Presentation and Workshop

- *2014 Goldschmidt* “Seasonal Variations in Nitrate Flux and Isotopic Composition in the Upper Illinois River Basin.” Conference presentation.

- *2014 AGU* "Nitrate Sources and Transport in the Upper Illinois River Basin Evaluated with Stable Isotope Ratios and SWAT Modeling." Conference presentation.
- 01/2014 Attended *Watershed Science Master Class*: the Hydrology Workshop held by CUAHSI (Consortium of Universities for the Advancement of Hydrologic Science), focusing on training in experimental design and modeling of watershed hydrologic and biogeochemical processes**.**

Publications

- Liu, H.Y., **Lin, J**., Zhang, M., Lin, Z., and Wen, T., (2008) Extinction of poorest competitors and temporal heterogeneity of habitat destruction. *Ecological Modeling*, 219: 30-38.
- Zhang, M., Yang, H., **Lin, J**., Gao, M., et al., (2008). Study of soil erosion of Dianchi Catchment using ^{137}Cs tracer and selected chemical properties. Ecology and Environment. *Ecology and Environment*, 17(6):2450-2457
- Wang, X., Yang, H., Zhao, Q., Liu, X., **Lin, J**., and Sang, L., (2009) Application of ^{137}Cs on the study of soil erosion of yellow brown earth in the mountainous area in Ningzhen District. *Journal of Soil and Water Conservation*, 2009(2):32-36
- **Lin, J**., Huang, S., Gonzalez-Meler, M., Böhlke, J.K., and Sturchio, N., (2014) Seasonal Variations in Nitrate Flux and Isotopic Composition in the Upper Illinois River Basin. *Goldschmidt Abstracts*, 2014 1459
- **Lin, J**., Yan, E., Demissie, Y., Böhlke, J.K., and Sturchio, N., (2014) Nitrate Sources and Transport in the Upper Illinois River Basin Evaluated with Stable Isotope Ratios and SWAT Modeling. *AGU Abstract*, 2014 H23G-0950

Journal articles in preparation or submission

- **Lin, J**., Huang, S., Böhlke, J.K., Gonzalez-Meler, M., and Sturchio, N.. Seasonal variations in nitrate flux and isotopic composition in the Upper Illinois River Basin.
- **Lin, J**., Yan, E., Demissie, Y., Sturchio, N., and Böhlke, J.K.. Modeling of nitrate sources, transport, and denitrification in the Upper Illinois River Basin: an application of SWAT.
- Sherif, M., **Lin, J**., Poghosyan, A., Abouelmagd, A., Sultan, M., Sturchio, N.C., Radium isotopes in groundwater of the southern Sinai Peninsula, Egypt.

Scholarships and Awards

2003-2006	College Scholarship Nanjing Normal University
2009	Excellent Graduate, Top Student Nanjing Normal University
2012	Knourek Field Study Scholarship; Provost and Deiss Awards University of Illinois at Chicago
2014	Graduate College Student Presenter and College Travel Awards University of Illinois at Chicago

Memberships and Affiliations

- AGU American Geophysical Union, 2012-present
- GSA Geological Society of America, 2012-present
- Terra Society (Student Organization at University of Illinois at Chicago), (2009-present)

Skills

- Software:

--In proficiency in ArcGIS, Microsoft Office (Word, Excel, Power Point)

- Instrument:

--In proficiency with α-Spectrometer, γ-Spectrometer, UV/Vis, GC-MS

- Programming language:

--In familiarity with R, MATLAB, Python

- Other skills:

--Laboratory analysis, field work

- Language

--English: native or bilingual proficiency

--Chinese: native proficiency