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Identifying Unknown Sources of Nitrate in Two Central Illinois Watersheds

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IDENTIFYING UNKNOWN SOURCES OF NITRATE IN TWO CENTRAL ILLINOIS WATERSHEDS

WILLIAM AUSTIN ANDREWS

36 Pages

Nitrate pollution is a major environment problem facing many agriculturally intensive areas around the world. In the midwestern USA, upstream tributaries to the Mississippi River via the Mackinaw and Illinois rivers, local excess nitrate can create problems with the safety of drinking water. In central Illinois, lakes, which are regulated and designated for use as municipal water supply, can periodically exceed EPA drinking water criteria for nitrogen. Lake Bloomington of the Money Creek watershed is the primary source of water for the City of Bloomington, whereas Evergreen Lake of the Six Mile Creek watershed serves as auxiliary supply. Both watersheds are dominated by row crop agriculture, primarily corn and soybean, with the main differences being Lake Bloomington has permanent residencies along the lakeshore that all function on septic waste systems. In this study, we collected 29 low-flow condition samples, taking necessary field parameters, analyzing ion concentrations, and analyzing the samples for $\delta^{15}N$ and $\delta^{18}O$ of nitrate. The combination of field parameters, ion data, and isotope ratios allows us to attempt identification of contributors of nitrate in this system and make deductions about the evolution of nitrate spatially. Results of this study suggest that contributions may indeed be from manure and septic waste and that denitrification processes were, at least for Evergreen Lake, occurring at the time of sampling.

KEYWORDS: nitrate, isotopes, denitrification, septic waste, fertilizer

IDENTIFYING UNKNOWN SOURCES OF NITRATE IN TWO CENTRAL ILLINOIS

WATERSHEDS

WILLIAM AUSTIN ANDREWS

A Thesis Submitted in Partial
Fulfillment of the Requirements
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2021

IDENTIFYING UNKNOWN SOURCES OF NITRATE IN TWO CENTRAL ILLINOIS

WATERSHEDS

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ACKNOWLEDGMENTS

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CHAPTER I: INTRODUCTION

Nitrate pollution is a major concern to water quality in agricultural lands due to fertilizer inputs; a problem that is quite significant in the Midwestern corn belt (Zhang et al. 2012). The Illinois River drains one of the largest corn-producing and nitrogenous fertilizers consuming areas in North America before it joins with the Mississippi River. Excess nitrate can compromise the safety of water bodies intended for use as municipal or human supply. Nitrate pollution is a problem that is incredibly significant in Illinois, a state that has a high population along with high agricultural crop output, which is achieved by being one of the highest fertilizer applying areas in North America (EPA 2014). The midwestern states' high nutrient loading to the streams is the main contributor to the Gulf of Mexico dead zone, which is also one of the largest in area in the world (Rabalais et al. 2002). The Illinois River is one of the largest inputs of nitrate pollution into the Mississippi River, but agriculture is not the only possible source (Royer et al. 2006). Nitrate pollution can enter a body of water through a multitude of sources, with the most significant sources being anthropogenic such as fertilizer runoff, animal manure, and human sewage (Ju et al. 2009). An important challenge for water quality management is to distinguish between the various potential sources of nitrate - fertilizer, manure, and human sewage in order to implement better remedial and preventative action.

When crucial drinking water sources exceed the Environmental Protection Agency's limit for nitrate, many people are put at a seemingly avoidable health-risk. According to an estimate by the USGS in 2015, over 73% of the water used each day in the United States comes from surface-water sources (Dieter et al. 2018). Excess nitrate in drinking water over 10mg/L $N-NO_3^-$ is known to cause methemoglobinemia, which can drastically reduce the amount of oxygen

carried by the hemoglobin; it is primarily a risk to infants and elderly who already have a weakened circulatory system or oxygen saturation problems (Camargo et al. 2006). More recently, excess nitrate has been linked to cancer, which can develop after prolonged or chronic intake of water with unsafe levels of nitrate (Ward et al. 2018).

Additionally, and particularly in Central Illinois, agricultural croplands have a series of tiles and drains in the subsurface to drain and move water in and out of the fields in order to drop the water table and vadose zone to keep the roots of crops dry. While this practice is necessary to make a big portion of Illinois arable for crop production, it essentially by-passes shallow and deep percolation that in turn bypasses denitrification by plants and microbes which inhabit the soil. The bypass of crucial steps in the flow of water causes nitrate to remain in the discharges of tile drain water before entering streams (Panno et al. 2008). Another major issue arises is that many streams have been 'improved' in the sense that they were dredged, riparian vegetation was removed, and the banks were cut to form an up-turned trapezoid. The trapezoidal shape moves water in the most efficient and fast manner, which again shortens the amount of time for vital biogeochemical processes to occur in stream, such as denitrification.

Six Mile Creek and Money Creek, both indirect tributaries of the Illinois and Mississippi Eivers, in Central Illinois share near-identical in agricultural land-use and dispersed rural residences (figure 1;) yet, their respective municipal supply reservoirs, Evergreen Lake and Lake Bloomington, present different water chemistries. Lake Bloomington is listed as an impaired water by Clean Water Act § 303(d) due to periodic exceedance of the EPA's 10mg/L safe drinking water limit for nitrate-nitrogen. When Lake Bloomington exceeds nitrate levels, water from Evergreen Lake is used to dilute the water from Lake Bloomington to an acceptable level before routing the water to the residents of Bloomington. Additionally, in 1996 both lakes had

aeration systems installed to help counteract stratification and periodic eutrophication caused anoxia (Raman et al. 1998). While Evergreen Lake has had similar issues in the past, it does not experience them it on a near-annual basis as Lake Bloomington does. The difference may be in the physical structure of the lakes themselves as Evergreen Lake is surrounded by forested parkland, while Lake Bloomington's shoreline has several dozen homes that operate on septic systems, which may be a significant contributor of Lake Bloomington's nitrate issues (Aravena et al. 1993). The Evergreen Lake-Six Mile Creek and Lake Bloomington-Money Creek watersheds' land use is   87% and 83% respectively (Lampo 2017). It is imperative that people have access to clean and safe water and in the case of the watersheds under investigation in this study nearly one hundred thousand people rely on Lake Bloomington for their drinking water.

As both Six Mile Creek and Money Creek watersheds have almost an identical percentage of land dedicated to row-crop agriculture, the two watershed's reservoirs should have relatively identical water chemistries, but they have a history of not being identical. It is imperative to determine nitrate sourcing in Lake Bloomington and Money Creek Watersheds in order to better plan and reduce the prevalence of the near-annual nitrate concentration exceedance.

Using Nitrogen and Oxygen Isotopes to Source Nitrate

Isotopes are an immense tool in the geosciences both radiogenic and stable. Radiogenic or radioactive isotopes undergo atomic decay and help geologists determine timescales whereas stable isotopes do not undergo decay and are extremely useful in the understanding of how things move and change over time. In the case of this study the ratio of $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ can offer insights on where nitrate came from and how that nitrate changes temporally and spatially. The process at play that has the greatest effect on stable isotope signatures over space and time is

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kinetic fractionation, a process more involved but very similar to sediment differentiation. Isotopic fraction in the nitrate system is primarily kinetically driven, meaning stable isotopes are separated due to differences in mass (Kendall 2000). Kinetic reaction rates depend on the ratios of the masses of the isotopes and their atomic properties. Bonds of the lighter isotopes are essentially weaker than those of their more massive counterparts, causing the less massive isotopes to react more readily thus, removing the lighter isotopes from the residual body, resulting in an enrichment of the more massive isotopes in the residual sample (Kendall, 2004).

Because of fractionation, biogeochemical processing of nitrate can be identified using distinctive isotopic signatures. Many, if not most, biologically driven reactions follow these kinetic fractionation principles based on the mass of the isotopes. Organisms will preferentially take up the less massive isotopes because they have weaker bonds and thus requires less energy for them to take in the lighter of the isotopes. With nitrate, the main biologically driven process of concern is plants and microbes that cause denitrification. Essentially with denitrification nitrate comprised of ^{14}N or ^{16}O is being preferentially taken up, leaving behind the un-utilized ^{15}N or ^{18}O in the residual. In water that has undergone denitrification, the concentration of nitrate in the water will be lesser but when you compare ^{15}N relative to ^{14}N, ^{15}N will be enriched relative to ^{14}N. Denitrification can be more accurately determined using a ratio of $\delta^{15}N_{NO3}$ relative to $\delta^{18}O_{NO3}$ and can be approximated at a 2:1 ratio (Divers et al. 2014).

Using a combination of both N and O isotopes in nitrate, we can also determine both the sources of nitrate and if any processing has occurred. Typical $\delta^{15}N_{NO3}$ values of sources are as followed; atmospheric NO_3^-: -10 ‰ to 15 ‰, NO_3^- fertilizer: -5 ‰ to 5 ‰, manure and septic waste: 0 ‰ to 15 ‰, soil NH_4^+: 2.5 ‰ to 7.5 ‰, and NH_4^+ in fertilizer and precipitation: -10 ‰ to 5 ‰. Typical $\delta^{18}O_{NO3}$ isotopic values of the sources are as follows; atmospheric NO_3^-: 30 ‰

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to 80 ‰, NO_3^- fertilizer: 15 ‰ to 25 ‰, manure and septic waste: -18 ‰ to 12 ‰, soil NH_4^+: -18 ‰ to 12, and NH_4^+ in fertilizer and precipitation: -18 ‰ to 12 ‰. Higher values of $\delta 18O_{NO3}$, 27.5 ± 27.5‰, are indicative of more direct sources of nitrate deposition such as NO3- fertilizers and atmospheric deposition which is due to a high degree of ^{18}O enrichment due to exchange of O atoms with ozone (O_3), which causes oxygen to be the main delimitator between direct and in-direct nitrate deposition (Hastings, 2003). The difference in values of $\delta^{15}N_{NO3}$ is more subtle and mainly serves to separate the ammonium rich sources such as NH4+ of fertilizers, soil, and precipitation from manure and septic system waste, however, all three sources appear to overlap in signatures at 2.5 ‰ to 5 ‰ $\delta^{15}N_{NO3}$, which complicates things slightly.

Isotopes have been successfully used to identify nitrate non-point and point sources (Kaushal et al. 2011). In North Carolina, isotopes indicated that the primary source of nitrate in a stream was from septic systems (Iverson et al. 2015). Enriched ^{15}N in groundwater indicated denitrification was impacting nitrate processing (Townsend et al. 2002) In the middle reaches of the Mississippi River, nitrate isotopes suggest that most of the NO_3^- in the river is either soil-derived or from synthetics fertilizers, and that denitrification in the river was significant with values as high as 55% (Panno et al. 2006). In highly populated and polluted waters of China, nitrate isotopes have been to determine source contributions in terms of bulk percentages and found that while fertilizer input was the overall main contributor amongst their sites but in addition how variable this percentages can be in different streams and parts of the lake (Liu et al. 2018).

Questions and Hypothesis

The objective of this study is to explore potential sources of nitrate in each watershed and lake using nitrate isotopic analysis of $\delta^{15}N$ and $\delta^{18}O$ of nitrate, to develop longitudinal nitrate

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concentration profiles for the two watersheds, and to compare watershed hydrofacies using ion concentration data. This study aims to answer the following questions: 1) What are the relative nitrate sources of the two watersheds and their respective reservoirs? 2) How do the nitrate concentration profiles of the two watersheds change longitudinally from their source to their reservoirs? 3) How do these watersheds compare to one another in terms of hydrofacies? To address question (1), isotope ratio data of $\delta^{15}N$ and $\delta^{18}O$ of nitrate will be used to distinguish differences in nitrate sources. Question (2) was addressed by recording field parameters (temperature, dissolved oxygen, pH, conductivity) and nitrate ion concentration data. Question 3 was determined by analyzing samples concentrations for cations and anions then assembling piper diagrams to distinguish hydrofacies. The goal of this study was to improve the understanding of potential sources of nitrate in these drinking water reservoirs and watersheds and how the water chemistry responds to the in-situ processing of nitrate. Additionally, it could potentially lay the groundwork for actions of remediation or prevention, particularly if the isotope sourcing shows residential septic or municipal sewage leakage. It is hypothesized that septic waste may be contributing to the near annual nitrate-nitrogen exceedance of Lake Bloomington.

CHAPTER II: METHODS

Study Area

The two watersheds of focus in this study, Six Mile Creek and Money Creek and their respective impoundment reservoirs Evergreen Lake and Lake Bloomington are almost entirely located within the confines of McLean County, Illinois except for a small fraction of Evergreen Lake and the final stretch of Six Mile Creek below the dam at Evergreen Lake. The land area the watersheds of Six Mile Creek and Money Creek encompass 104 km^2 and 174 km^2 respectively. Both watersheds empty into the Mackinaw River, with Money Creek joining upstream roughly 7.2 km east of Six Mile Creek. From our area of study, the Mackinaw River then travels through portions of Woodford and Tazewell Counties before eventually converging with the Illinois River. Lake Bloomington of Money Creek was built in 1929 as a water supply reservoir for the City of Bloomington, McLean County, Illinois and cover an area of 2.3 km^2 with an average depth of 5.8 m and a max depth of 16.8 m and is currently the primary source of water for the city. Evergreen Lake of Six Mile Creek Watershed was constructed in 1971 and was intended to serve as a supplemental and emergency water supply for the City of Bloomington and covers an area of 3.2km^2 with an average depth of 4.4 m and a maximum depth of 11 m.

Both watersheds originate and are primarily fed from tile drainage resulting from regional agricultural practices. These regional practices are typically the row-cropping of corn and soybean in a multi-year rotation. Land use in Money Creek-Lake Bloomington watershed is 83% row crop agriculture with roughly 50% covered by corn and 33% covered by soybean. Similarly, Six Mile Creek-Evergreen Lake watershed land use is 87% row crop agriculture. Both watersheds are designated for use by the City of Bloomington, located south and southwest of the watersheds in central McLean County, Illinois. Fertilizers are applied late fall or early winter,

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either as the sole application or part of a biannual fertilization that include a spring application. The general fertilizer that is utilized in the corn belt is anhydrous ammonia. Site coordinates, elevation, and stream length upstream from the Mackinaw River for both watersheds was determined in Google Earth Pro, following the middle of the stream for the entirety of both streams to determine total upstream distance (table 1).

Table 1: Stream Site Descriptions. We sampled six sites on Money Creek and four sites on Six Mile Creek. All sites were located at road crossings. Sample IDs are ordered from upstream to downstream.

Body	Sample ID	Site #	Decimal Degrees	Elevation (m)	Length (km)	Description
			Stream Site Descriptions			
Money Creek	$1	1	40.488365, -88.764656	250	44.3	Agriculture Ditch
	$2	2	40.513892, -88.806875	243	38.9	Clear Trickle
	$3	3	40.538965, -88.863352	237	30.5	Severe Algal Growth, livestock.
	$4	4	40.560700, -88.877231	233	26.2	Large, Turbid
	$5	5	40.569154, -88.445009	231	24.5	Deep, Turbid
	$6	6	40.594041, -88.888790	227	18.2	Shaded, Turbid
	$7	7	40.605351, -88.898410	223	15.4	Wide Turbid
Six Mile Creek	6mc4	4	40.576542, -88.977154	233	18.1	Small Clear Stream
	6mc5	5	40.588564, -88.983511	229	16.5	Medium Clear Stream
	6mc6	6	40.605375, -88.002825	225	12.9	Large Clear Stream
	LEin	Evergreen Inlet	40.620885, -89.017083	219	8.4	Mouth into Evergreen Lake

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Table 2: Lake Locations and Depth of Sample. We collected 9 samples across 5 locations in each lake, with one sample collected in the deepest portion of the lake near the dam, and 2 samples collected at each of the remaining four locations with on surface sample and one below the photic zone.

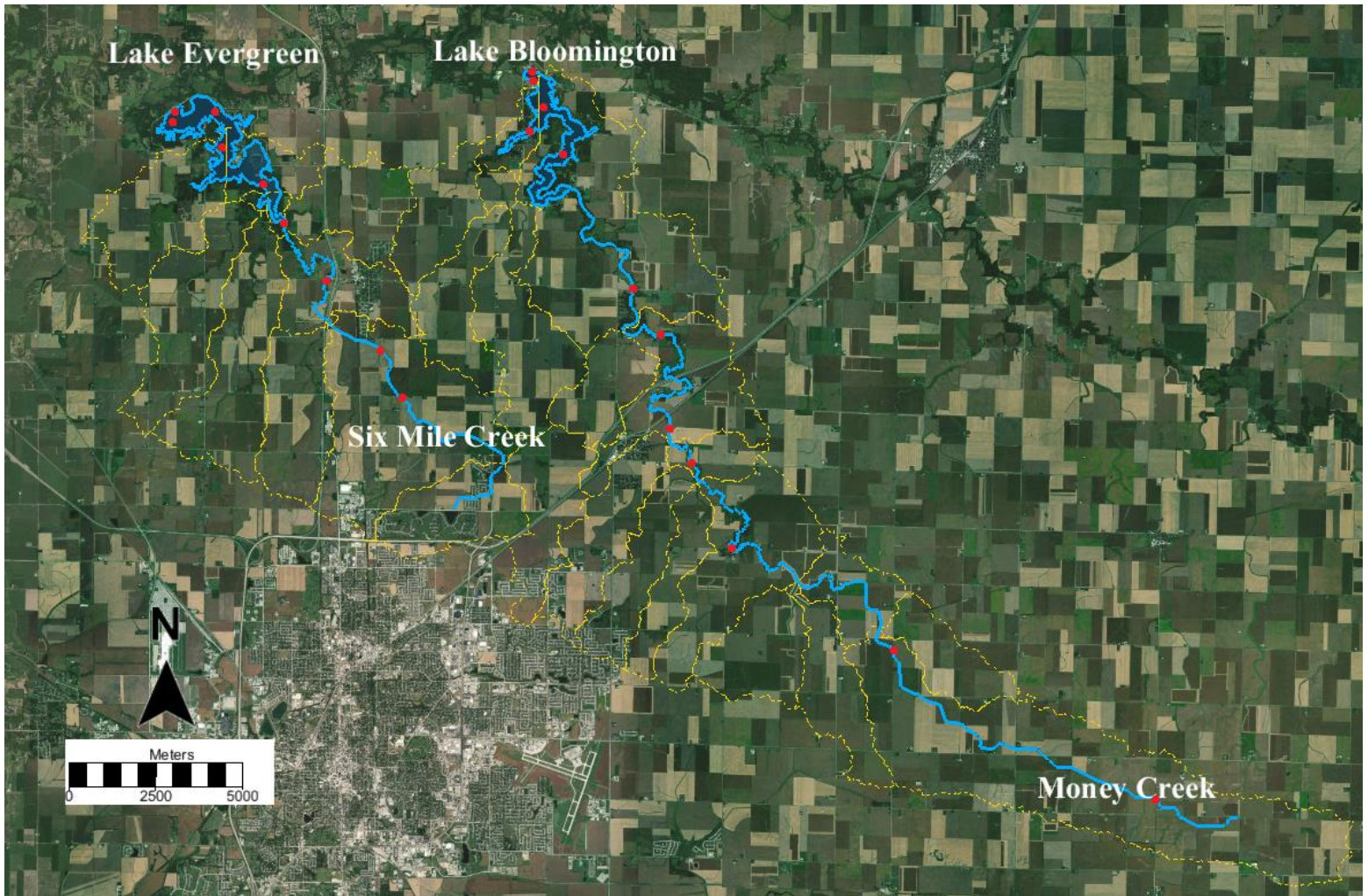| Lake Locations & Depth			
		Decimal Degrees	**Depth**
Lake	**ID**		m
Lake Bloomington	Shallow-3	40.63887, -88.9255	0.0
	Deep-3		1.5
	Shallow-4	40.64617, -88.9334	0.0
	Deep-4		1.5
	Shallow-2	40.65152, -88.9287	0.0
	Deep-2		2.0
	Shallow-1	40.66038, -88.9349	0.0
	Deep-1		2.0
	Deep Near Dam	40.64923, -89.05505	8.0
Evergreen Lake	Shallow-3	40.63103, -89.026	0.0
	Deep-3		1.0
	Shallow-2	40.63889, -89.0419	0.0
	Deep-2		1.5
	Shallow-4	40.64954, -89.0413	0.0
	Deep-4		3.0
	Shallow-1	40.64785, -89.0553	0.0
	Deep-1		3.0
	Deep Near Dam	40.66120, -88.93451	**_7.5_**

Figure 1: Watershed map of study area. Bloomington-Normal metropolitan area is in the

bottom left of this image.

Field Sampling

Field sampling was conducted as a team on the 26th of September 2020. Sampling of the streams and lakes along with measurements of stream discharge were executed simultaneously to capture data in as small of a time frame as possible. In total 29 samples, all with a volume of one (1) liter were collected, labeled, and immediately placed on ice. Of the 29 samples collected there were: 7 samples collected from Money Creek, 4 samples collected from Six Mile Creek, 9 samples collected from Lake Bloomington, and 9 samples collected from Evergreen Lake. Of the 9 samples taken at each reservoir, 5 of those samples were collected below the photic zone which was determined using a Secchi disc to determine depth of light extinction. For all samples collected a field alkalinity titration was executed using a Hach Digital Titrator. Additionally, for all sample locations field parameters (temperature, dissolved oxygen, conductivity, pH) were measured using a YSI ProPlus. Sample filtering was not conducted in the field as all samples were promptly placed on ice then moved to a freezer when sampling was concluded. Discharge measurements using velocity and area were conducted using a Sontek Flowtracker flow meter. Creek samples were collected off public bridges to avoid land access requests and trespassing and sample was pulled up using a peristaltic pump. Lake samples were conducted off a boat using a Van Dorn sampler for deep water collected and a simple grab method for surface samples. Site descriptions (table 1, table 2;) was recorded in the field at the time of sampling.

Sample Analysis

Samples were thawed in a water bath and filtered using a 1 µm glass fiber filter (Pall Corporation). After thawing,120 mL of sample was transferred into 60 mL Nalgene bottles. Another 60 mL of sample was filtered at 0.2 µm with Whatman nylon membrane filters. All transferred and filtered samples were relabeled to indicate their analytical destination and refrozen. The set filtered at 0.2 microns were packaged in dry ice and shipped to University of California-Davis Stable Isotope Facility for nitrate isotope analysis utilizing a bacterial denitrifier method where nitrate was converted to nitrous oxide and analyzed on a gasbench mass spectrometer (Sigman et al. 2001, Casciotti et al, 2002). The other samples were analyzed at Illinois State University's Laboratory for Environmental Analysis. Anions were analyzed on a Dionex ICS-1100 Ion Chromatograph. Cations were analyzed on a Perkin Elmer Inductively Coupled Plasma. Nitrate nitrogen concentrations were additionally run on a Lachat Flow Injection Analyzer for enhanced accuracy because concentrations were low. Trilinear Piper Diagrams were made using the US Geological Survey's GW_Chart software where the nitrate concentration was added to the chloride concentration for a sum of the two as to include them in a piper diagram (Hackley et al. 2007). All remaining figures and statistics were made with Microsoft Excel. Total dissolved solids (TDS) was calculated using the cation and ion results by adding all major ions (Fl^-, Cl^-, Br^-, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, and HCO_3^-).

CHAPTER III: RESULTS

Parameter Results

The geochemical assessment of low-flow and low-fertilizer input samples displayed relatively similar results across most measured and analyzed parameters (table 3). The air temperature the day of sampling on September 26, 2020 saw a low temperature of 16° C before sunrise and a high temperature of 28° C from roughly 3pm to 5pm. The last measurable amount of precipitation before sampling occurred on September 12th which was 20mm of rain. Stream discharges were measured for all locations with a measured maximum discharge of 0.075 m³/s. Water temperature ranged from 16.3°C to 24.7°C in the streams with an average of 19.6°C and from 15.2°C to 21.2°C with an average of 20.4°C. The difference between the average surface samples from the lakes and the below photic zone samples was 0.6°C, which shows that there was some degree of a temperature gradient in the lake water columns with depth.

Table 3: Stream Parameters. Basic water quality parameters are provided in order from upstream to downstream for each stream.

Stream Parameters						
		Temp	DO	DO	SpC	TDS
Body	**ID**	(°C)	(%)	(mg/L)	μS/cm	ppm
Money Creek	$1	17.8	28.7	2.65	772.0	579.110
	$2	18.6	27.4	2.50	494.1	378.469
	$3	16.3	6.7	0.64	489.5	366.841
	$4	18.3	77.8	7.46	508.8	384.001
	$5	19.9	94.5	8.84	637.0	452.858
	$6	16.9	26.9	2.58	544.8	400.558
	$7	17.5	53.5	5.06	937.0	701.595
Six Mile Creek	6mc4	23.1	79.0	6.72	1029.0	728.796
	6mc5	24.7	113.4	9.29	652.0	530.525
	6mc6	20.5	88.0	7.86	633.0	459.259
	LEin	22.1	116.6	10.10	512.8	371.812
Minimum		16.3	6.7	0.64	489.5	366.841
Maximum		24.7	116.6	10.10	1029.0	729.796
Average		19.6	64.8	5.791	655.5	486.802

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Table 4: Lake Parameters. Basic water quality parameters for Lake Bloomington and

Evergreen Lake ordered relatively upstream from reservoir impoundment.

Lake Parameters							
		Temp	**DO**	**DO**	**SpC**	**TDS**	**Depth**
Body	**ID**	(ºC)	(%)	(mg/L)	µS/cm	ppm	(m)
Lake Bloomington	Shallow-3	20.9	106.4	9.50	358.5	265	0.0
	Deep-3	20.6	94.7	8.44	359.7	276	1.5
	Shallow-4	20.6	110.0	9.78	356.6	255	0.0
	Deep-4	20.4	97.7	8.81	256.0	268	1.5
	Shallow-2	21.1	111.	9.90	355.5	264	0.0
	Deep-2	20.8	98.5	8.81	356.8	261	2.0
	Shallow-1	21.2	115.0	10.00	356.0	278	0.0
	Deep-1	21.1	106.6	9.48	356.1	284	2.0
	Deep Near Dam	20.9	100.2	8.95	357.5	180	8.0
Evergreen Lake	Shallow-3	20.1	77.5	7.09	363.0	279	0.0
	Deep-3	20.1	77.5	7.09	363.0	279	1.0
	Shallow-2	20.2	86.0	7.74	364.0	267	0.0
	Deep-2	20.6	78.2	7.02	365.0	259	1.5
	Shallow-4	20.7	113.0	9.89	362.0	259	0.0
	Deep-4	20.7	97.7	8.65	362.0	254	3.0
	Shallow-1	20.6	108.5	9.77	363.0	267	0.0
	Deep-1	20.6	105.5	9.44	362.0	260	0.0
	Deep Near Dam	15.2	11.5	1.13	522.6	385	3.0
Minimum		15.2	11.5	1.13	355.5	254	0.0
Maximum		21.2	115.0	10.00	522.6	385	8.0
Average		20.4	94.2	8.42	369.0	274	1.3

Major Ion Results

The most variable of all the chemical constituents was chloride with a minimum value of 22.104 mg/L and a maximum of 298.725 mg/L. The constituent with the least variability in this sample set was fluorine with a range of 0.202 mg/L to 0.415 mg/L and an average of 0.294 mg/L. Nitrate-nitrogen concentrations were relatively consistent with a variance of +/- 0.48 and an average of 0.12 mg/L nitrate-nitrogen. However, all samples had a nitrate concentration range between 0.0 and 0.2 N-NO3 mg/L except for sample sites Money Creek 7 and Six Mile Creek 6. Average nitrate-nitrogen concentrations for both Six Mile Creek and Money Creek were identical at 0.12 mg/L with a standard deviation of 0.15 and a standard error of 0.05. In terms of total dissolved solids (TDS), there was downstream correlation with decreasing TDS concentration which is displayed in tables 3 and 4. For the most part we see higher ion concentrations in the streams than in the lakes for all measured ions except fluoride, bromide, and potassium.

Our results showed that there was a general increase in nitrate concentration downstream figure 2, table 3). The two highest nitrate nitrogen concentrations of 0.485 N-NO3 mg/L at Six Mile Creek and 0.355 mg/L N-NO3 at Money Creek both occurred at the furthest downstream point in the creeks, before reaching the lakes. There was a discernable difference in nitrate concentrations between the streams and the lakes (table 5, table 6, figure 2). The datapoint for Six Mile Creek between 5,000 m and 10,000 m was essentially the mouth of Six Mile Creek emptying into Evergreen Lake and is best described as somewhat of a marshy mudflat that is periodically flooded by the lake.

The average nitrate nitrogen concentrations were on average highest in Lake Bloomington with an average concentration of 0.153 mg/L N-NO3 with a standard deviation of

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0.040 and a standard error of 0.009. Evergreen Lake, Six Mile Creek, and Money Creek have average nitrate nitrogen concentration of 0.086, 0.123, and 0.124 mg/L respectively. With Six Mile Creek and Money Creek having nearly identical concentrations of nitrate on average, it should be the case that the two lakes have similar average concentrations. Nitrate nitrogen concentrations from samples below the photic zone and samples at the surface are virtually identical with average concentrations of 0.120 mg/L N-NO3 and 0.119 mg/L N-NO3 respectively which indicates that there is likely not much a concentration gradient of nitrate with depth in the lakes. Analysis of anions and cations across all samples indicated that for both watersheds have a magnesium bicarbonate type hydrofacies.

Table 5: Stream Ion Concentrations. Water chemistry is ordered from upstream to downstream for each stream.

Stream Ion Concentrations (mg/L)												
Body	ID	F$^-$	Cl$^-$	Br$^-$	N-NO3	SO$_4^{2-}$	Ca^{2+}	Na$^+$	K$^+$	Mg^{2+}	CaCO$_3$	HCO$_3^-$	Charge Balance Error
Money Creek	$1	0.23	80.8	0.00	0.064	15.1	43.1	24.6	4.90	46.8	298	364	34%
	$2	0.42	39.6	0.00	0.008	6.2	31.1	13.6	10.41	34.3	199	243	46%
	$3	0.35	33.5	0.14	0.060	13.6	31.5	11.0	3.92	25.1	203	248	42%
	$4	0.40	42.4	0.14	0.064	11.8	25.7	18.3	4.22	29.7	206	251	39%
	$5	0.35	105.0	0.20	0.067	24.7	23.5	35.5	4.48	29.8	188	229	13%
	$6	0.21	71.6	0.00	0.119	16.5	37.3	28.8	5.65	20.8	180	220	28%
	$7	0.32	210.7	0.02	0.485	26.2	35.0	80.2	5.63	39.4	249	304	8%
Six Mile Creek	6mc4	0.36	298.7	0.37	0.072	65.2	23.8	81.7	4.46	44.0	173	211	-11%
	6mc5	0.32	72.4	0.22	0.029	102.0	23.7	22.8	3.42	39.8	218	266	5%
	6mc6	0.26	80.9	0.02	0.017	42.7	17.4	24.6	3.74	36.5	199	243	17%
	LEin	0.29	75.8	0.24	0.036	28.6	17.0	24.1	4.02	24.1	162	198	11%
Minimum		0.21	33.5	0.00	0.008	6.2	17.0	11.0	3.42	20.8	162	198	-11%
Maximum		0.42	298.7	0.37	0.485	102.0	43.1	81.7	10.41	46.8	298	364	46%
Average		0.32	101.0	0.12	0.123	32.0	29.0	33.2	4.99	33.7	207	252	21%

Table 6: Lake Ion Concentrations. Ion concentrations, depth of sample, and charge balance error for all samples across both lakes.

| Body	ID	Fl⁻	Cl⁻	Br⁻	N-NO3	SO₄²⁻	Ca²⁺	Na⁺	K⁺	Mg²⁺	CaCO₃	HCO₃⁻	Depth (m)	Charge Balance Error
						Lake Ion Concentrations (mg/L)								
Lake Bloomington	Shallow-3	0.24	25.5	0.00	0.116	13.1	24.4	6.9	3.73	15.7	144	176	0.0	38%
	Deep-3	0.23	25.5	0.00	0.113	13.2	26.0	7.4	3.83	19.1	148	181	1.5	41%
	Shallow-4	0.23	22.4	0.03	0.171	13.0	22.1	6.3	3.58	11.3	144	176	0.0	36%
	Deep-4	0.31	25.7	0.00	0.168	13.2	24.5	7.3	3.82	18.9	143	174	1.5	40%
	Shallow-2	0.27	25.1	0.00	0.158	13.8	23.3	7.4	3.84	19.2	140	171	0.0	39%
	Deep-2	0.22	22.1	0.00	0.162	11.8	22.3	6.2	3.58	11.7	150	183	2.0	38%
	Shallow-1	0.33	28.5	0.14	0.166	18.7	25.2	7.4	3.82	17.5	144	176	0.0	34%
	Deep-1	0.35	25.3	0.29	0.149	13.5	23.4	7.1	3.80	18.0	158	192	2.0	38%
	Deep Near Dam	0.25	27.3	0.00	0.174	19.8	26.3	7.7	3.87	19.0	144	175	8.0	36%
Evergreen Lake	Shallow-3	0.25	34.5	0.04	0.062	16.9	23.5	10.6	3.94	14.6	143	174	0.0	29%
	Deep-3	0.33	32.8	0.47	0.071	17.2	22.2	10.3	3.98	14.7	143	174	1.0	29%
	Shallow-2	0.30	32.0	0.26	0.083	26.7	21.7	10.3	3.97	14.7	129	157	0.0	24%
	Deep-2	0.29	30.7	0.17	0.078	16.2	23.1	10.2	3.96	14.3	131	160	1.5	32%
	Shallow-4	0.30	32.0	0.23	0.094	13.8	22.7	10.1	4.03	16.2	131	160	0.0	33%
	Deep-4	0.33	32.1	0.34	0.085	17.0	16.1	10.1	3.99	13.2	132	161	3.0	23%
	Shallow-1	0.32	31.3	0.21	0.102	17.5	26.4	10.3	4.00	16.5	132	160	0.0	34%
	Deep-1	0.30	33.4	0.19	0.090	18.4	26.4	10.3	4.00	16.5	124	151	3.0	32%
	Deep Near Dam	0.20	34.4	0.02	0.111	17.4	19.1	10.5	4.01	15.9	232	283	7.5	26%
Minimum		0.20	22.1	0.00	0.062	11.8	16.1	6.2	3.58	11.3	124	151	0.0	23%
Maximum		0.35	34.5	0.47	0.174	26.7	26.4	10.6	4.03	19.2	232	283	8.0	41%
Average		0.28	28.9	0.13	0.120	23.3	23.3	8.7	3.88	16.0	145	177	1.3	33%

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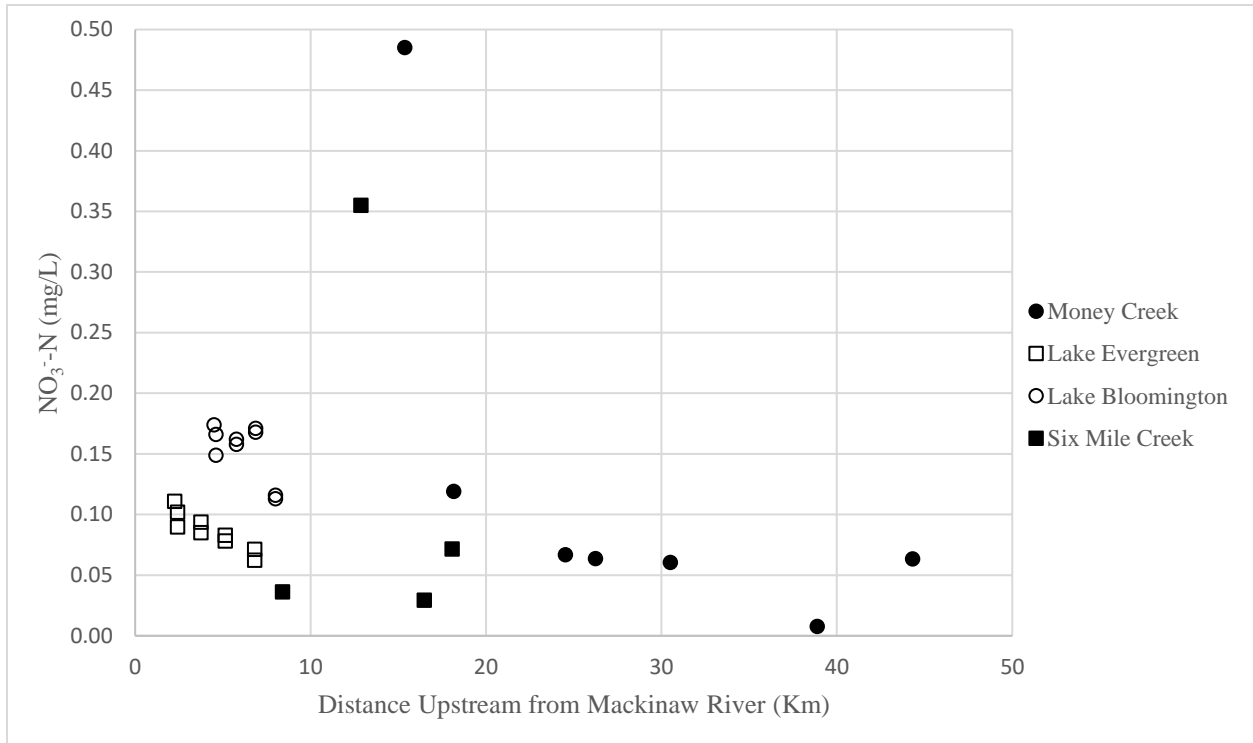
Figure 2: Nitrate concentrations in the lakes and streams going upstream from the

Mackinaw River.

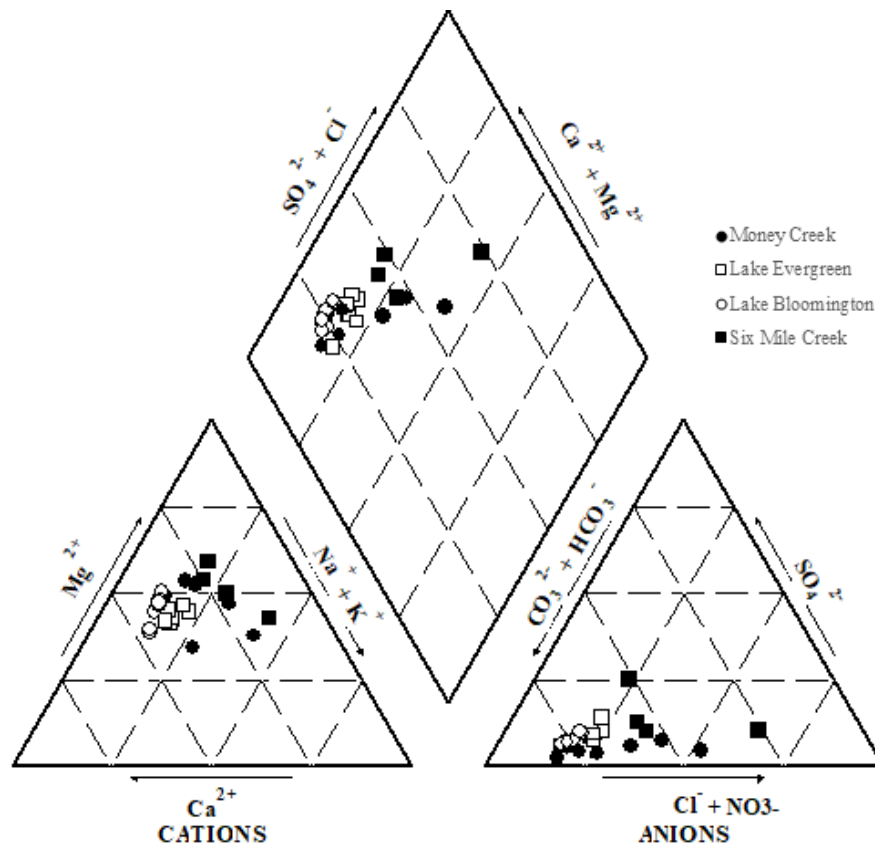**Figure 3: Piper Diagram showing the major ion geochemistry of the lakes and streams.**

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Isotope Results

Values of $\delta^{15}N_{NO3}$ ranged from 1.42 ‰ to 13.46 ‰ in the streams and 1.74 ‰ to 8.52 ‰ in the lakes with averages of 7.92 ‰ and 4.82 ‰ respectively. Values of $\delta^{18}O_{NO3}$ ranged from 0.03 ‰ to 4.67 ‰ in the steams and -8.17 ‰ to 2.88 ‰ in the lakes with averages of 2.54 ‰ and 1.18 ‰ respectively. Because of the extremely low concentrations of nitrate across a portion of samples, some samples were below the limit of quantification of roughly 0.06 mg/L NO3-N which increases standard deviation and greatly reduces accuracy of isotope analysis, such samples are reported in Tables 6 and Tables 7 with red text and an asterisk. The variance between $\delta^{15}N_{NO3}$ between both the streams and lakes was +/- 12.04 ‰ whereas the variance of $\delta^{18}O_{NO3}$ from both streams and lakes is +/- 4.64 ‰. The isotope mixing model (figure 4;) was based off previously established ranges of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ in nitrate sourcing identification and includes denitrification vectors (Kendall et al. 2007).

Table 7: Stream Isotope Results. $\delta^{15}N_{Air}$ and $\delta^{18}O_{VSMOW}$ of nitrate for Money and Six Mile Creek.

Body	ID	Site #	$\delta^{15}N_{Air}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
			Stream Isotope Ratios	
Money Creek	$1*	1	9.01*	10.43*
	$2*	2	3.47*	24.08*
	$3*	3	10.63*	14.76*
	$4*	4	9.47*	10.72*
	$5*	5	10.68*	20.91*
	$6	6	1.42	0.03
	$7	7	13.46	2.91
Six Mile Creek	6mc4*	4	1.96*	8.31*
	6mc5*	5	8.70*	13.99*
	6mc6	6	8.90	4.67
	LEin*	Evergreen Inlet	8.69*	20.90*
All	Minimum		1.42	0.03
	Maximum		13.46	24.08
	Average		7.85	11.97
Above LOQ	**Minimum**		**1.42**	**0.03**
	Maximum		**13.46**	**4.67**
	Average		**7.92**	**2.54**

(* denotes below LOQ, Limit of Quantification)

Table 8: Lake Isotope Results. $\delta^{15}N_{Air}$ and $\delta^{18}O_{VSMOW}$ of nitrate for Evergreen Lake and Lake Bloomington. (* denotes below LOQ, Limit of Quantification)

| Lake Isotopes Ratios			
		$\delta^{15}N_{Air}$	$\delta^{18}O_{VSMOW}$
Body	**ID**	(‰)	(‰)
Lake Bloomington	Shallow-3	5.74	2.44
	Deep-3	5.88	2.88
	Shallow-4	7.34	0.98
	Deep-4	7.39	2.43
	Shallow-2	6.11	2.37
	Deep-2	5.68	2.50
	Shallow-1	5.04	1.63
	Deep-1	5.74	1.17
	Deep Near Dam	5.54	0.58
Evergreen Lake	Shallow-3*	1.97*	6.42*
	Deep-3*	2.91*	6.42*
	Shallow-2	1.91	-5.91
	Deep-2	1.74	-2.66
	Shallow-2	2.01	-4.45
	Deep-2	2.01	-7.17
	Shallow-1	3.15	-3.07
	Deep-1	3.38	-8.17
	Deep Near Dam	8.52	-4.43
All	Minimum	1.74	-8.17
	Maximum	8.52	6.42
	Average	4.56	-0.34
Valid	**Minimum**	**1.74**	**-8.17**
	Maximum	**8.52**	**2.88**
	Average	**4.82**	**-1.18**
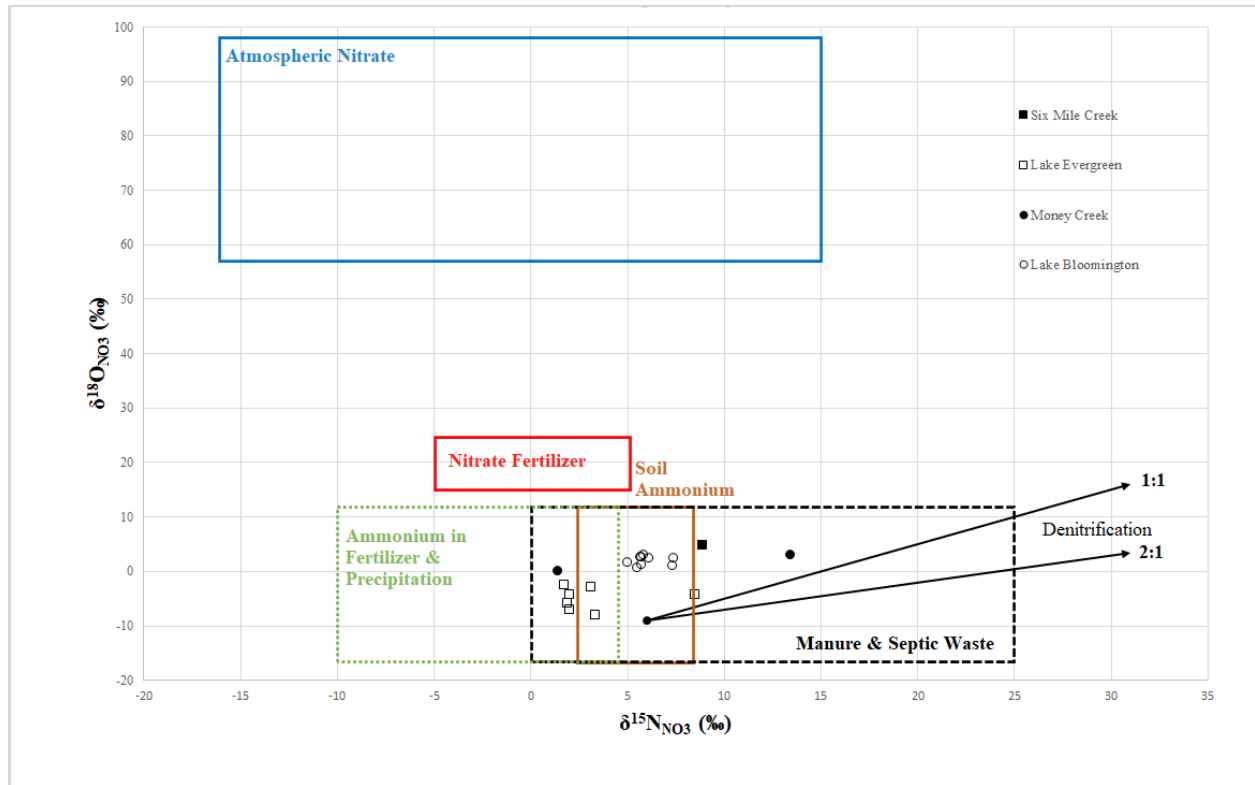
Figure 4: Isotope ratio analysis for nitrate. Boxes represent the approximate sources of nitrate based off the isotopic ratio of nitrate, based off established model from Kendall et al. (2007). The two vectors display typical fractionation slopes of 2:1 and 1:1during denitrification of nitrate with initial $\delta^{15}N$ = +6‰ and $\delta^{18}O$ = -9‰ (Kendall et al. 2007).
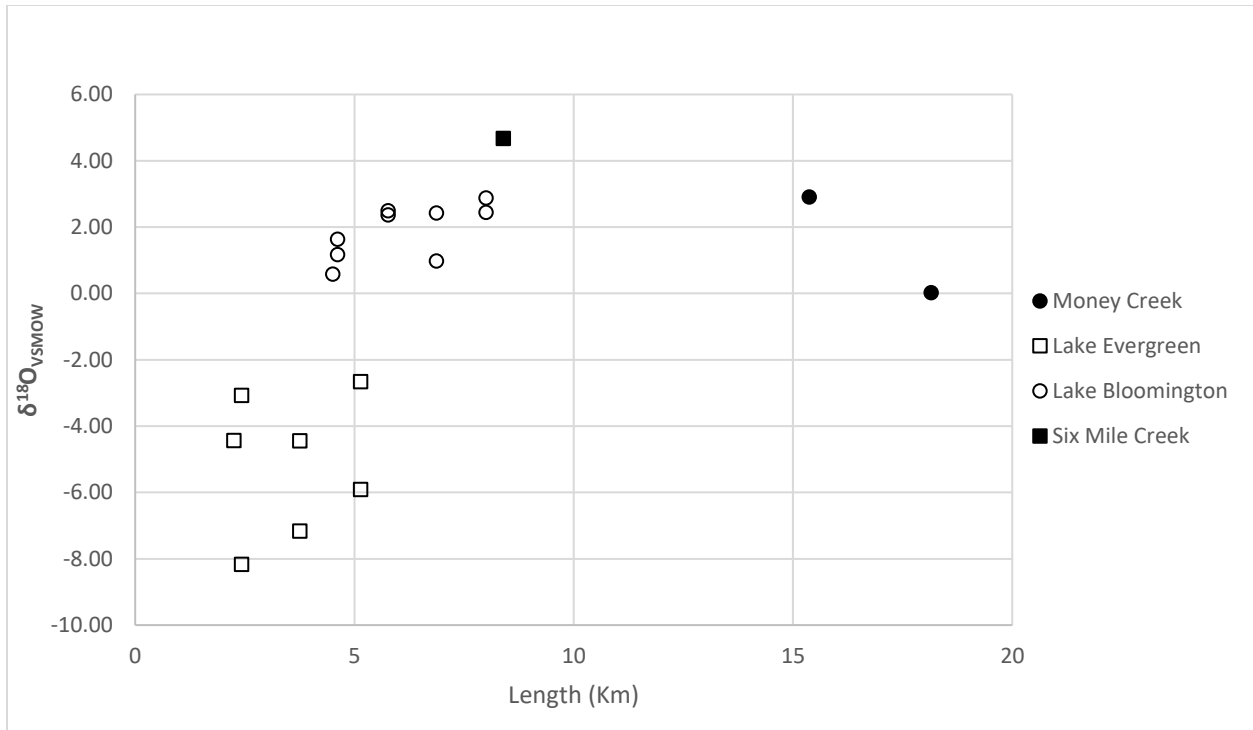
Figure 5: δ¹⁸O value of nitrate vs location upstream from Mackinaw River.

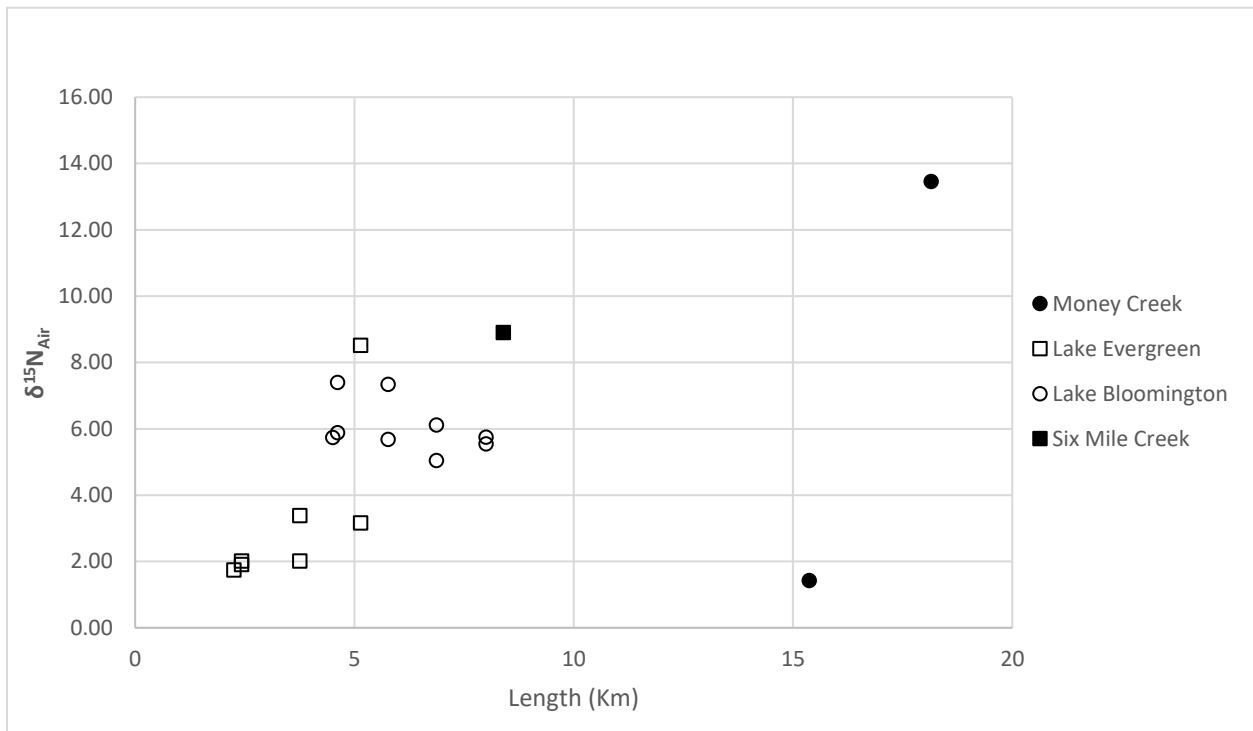**Figure 6: δ¹⁵N of nitrate vs location upstream from Mackinaw River.**

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CHAPTER IV: DISCUSSION

The general decrease in total dissolved solids can likely be attributed to dilution by mass load increase. The TDS data also suggests that during the low-flow drought-like condition samples did not have much if any interaction with groundwater, particularly in the downstream portions before reaching the lakes, as the downcutting of the stream cuts into the water table. In order to have determined whether it is groundwater that is causing this downstream change in TDS, groundwater samples would have needed to have been taken spatially during the sampling. The maximum measured discharge for our sampling in late September was 0.075 m^3/s which was less than the eight-month minimum discharge of 0.115 m^3/s that was measured in the same month four years prior (Lampos, 2017). This is an important aspect as not only is this typically the driest portion of the year for this region, but the low discharges captured in this study were much less than previous studies conducted on these streams.

The range of chloride concentrations captured in the streams is expected as road salts are applied to roads in the winter, and long-term use and frequent exposure to road salts will cause retention and concentrations will build up over time (Findlayp et al. 2011). This retention of road salts stabilizes chloride concentrations in the watersheds temporally (Oberhelman & Peterson 2020). The range of chloride concentrations in the lakes are considerably less variable than in the stream and had average concentration that is nearly one quarter of the concentrations of the streams. This can be seen in the specific conductivity data as the streams had more variability and an average that was nearly twice that of the lakes. The upper reaches of the streams had the highest specific conductivity, and gradually decrease downstream and through the lakes, specific conductivity may be making an argument that we are not seeing major groundwater interaction as in theory, groundwater entering the stream should have higher TDS and thus higher

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conductivity relative to the surface waters. Because of the disagreement on the aspect of major groundwater interaction occurring between the chloride concentrations and the specific conductivities, it appears that chloride may getting retained by soils and diffused more slowly over time than previous studies have shown.

At Money Creek sample site 3, dissolved oxygen concentration was 0.64 mg/L, which was the lowest dissolved oxygen concentration seen across all samples, with the near-dam sample at Evergreen Lake having a concentration of 1.13 mg/L being the next lowest. This location, at the time of sampling, was directly downstream from a small herd of cattle and a few horses and had significant algal growth in both visible directions from the sampling location. The low dissolved oxygen concentration was most likely caused by an excess of decomposing organic matter resulting from algal eutrophication, which consumes oxygen thus lowering the availability of dissolved oxygen (Nguyen et al. 2016). While the sample was collected during the daytime, the severe algal growth was thick enough to block significant amounts of sunlight and the presence of a small forest surrounding this stretch of the stream further reducing the amount of sunlight available to plants and microbes for transpiration and respiration. Excluding Money Creek samples 1-3 and 6, and the near dam deep water sample of Evergreen Lake, all samples have dissolved oxygen concentrations that are considered oxic, or greater than 2-3 mg/L concentration of dissolved oxygen (Senn et al. 2016). Anoxic conditions are present when dissolved oxygen concentrations are less than 0.5 mg/L dissolved oxygen which is slightly less than the lowest dissolved oxygen concentration we had across our samples (Warner and Arnold, 2010.) Denitrification occurs in a reducing environment characterized by anoxic (low-dissolved oxygen) conditions or high levels of hydrogen sulfide or methane but denitrification can also occur in anoxic microsites in oxygenated sediment (Brandes and Devol, 1997).

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The results of the Piper diagram (figure 3;) indicate that there was not a major evolution in water chemistry as we move downstream as for the most part all the samples plotted together in a group. However, you can see a slight difference in the distribution between the streams and lakes in terms of their individual constituents. For example, on the bottom right plot of the piper diagram, it is readily seen that chloride percentages display a wide range. This wide difference in chloride concentration can also be seen in the diamond plot that displays both cations and anions. The piper diagram indicates that both watersheds display calcium-magnesium bicarbonate type waters which display similar results as a study conducted in the southwestern Illinois sinkhole plain which was directly comparing spring water discharge with manure and septic waste (Hackley et al. 2007). The results displayed in the trilinear piper diagram are also relatively consistent with regional surface geology with is made up of glacial sediments mostly clayey to silty till with some pockets and lenses of sand and gravel that exist within the watersheds (ISGS 1979).

Nitrate concentrations in the streams were very low on average, even lower than normal as a previous study conducted on these watersheds during autumn baseflow conditions found average concentrations for Six Mile and Money Creek to be 7.50 mg/L N-NO3 ± 0.38 and 10.2 mg/L N-NO3± 0.57 respectively (Lampos 2017). Money Creek sample site 7 had a measured nitrate concentration of 0.485 mg/L N-NO3 which was four times higher than the next highest concentration on Money Creek which was sample site 6 at 0.119 mg/L N-NO3and 1.37 times higher than the highest nitrate concentration found in Six Mile Creek. Between Money Creek site 6 and site 7 is a rural neighborhood with several dozen homes which operate on septic waste, which may be an explanation as to why the isotopic ratios of nitrate are more enriched in $\delta^{18}O_{NO3}$ and plotted in the manure and septic waste box (figure 4). Similarly, between site 5 and 6 on Six

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Mile Creek lies the outskirts of the town of Hudson, Illinois, and a few rural homes east of Six Mile Creek and west of Interstate 39. The nitrate concentration spikes for Money Creek site 7 and Six Mile Creek site 6 appear to likely be a result of private septic sewage, or potentially even inadequate or deteriorating sewage systems, infiltrating that surface water as suggested by the isotopic mixing model (figure 4). The high nitrate concentrations for Money Creek site 7 and Six-Mile Creek site 6 appear abnormal when compared longitudinally with the other 27 nitrate concentrations measured in this study (figure 2).

Nitrate concentrations across both lakes were less variable and appear to be a result of more constant volume and mixing which occurs in the lakes as compared to the more variable flows of the streams. Nitrate concentrations for the lakes were also low, with Lake Bloomington having slightly higher concentrations than Evergreen Lake (figure 2). But the nitrate concentrations for both lakes are still much less than the highest concentration sample sites along both creeks and as both those sites were the last sample locations before the stream joined the lake there may be something affecting these values in that stretch between the last sample site and the lakes. Some of these processes could include denitrification occurring within the stream waters themselves or from the interaction of groundwater with the stream which in concept the groundwater would have undergone some degree of denitrification becoming more positive or enriched in the isotopic ratios of nitrate constituents at a 1:1 or 2:1 ratio (Kendall 2007). If major groundwater interaction were occurring between Money Creek site 7 and Six Mile Creek site 6, we would expect to see more positive isotopic ratios in those samples collected in the lakes than in than the two stream samples which plotted in the manure and septic waste box in the isotopic analysis (figure 4). However, the isotopic analysis shows that the ratios of collected samples from the lakes are more negative in $\delta^{15}N_{NO3}$ than their stream's high concentration counterpart

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and slightly more negative in $\delta^{18}O_{NO3}$ which offers a strong argument that denitrification did not occur between those final stream sites and the lakes nor did major groundwater interaction.

Additionally, for the lake samples, $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ ratios are more positive or enriched for the samples collected in Lake Bloomington than for the samples from Evergreen Lake, except for one the deep water near dam sample at Evergreen Lake (pSDA) which is more enriched in $\delta^{18}O_{NO3}$ than any point in Lake Bloomington. This point at Evergreen Lake likely experienced isotopic fractionation due to denitrification, which will enrich the sample isotopically in both $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$. The denitrification vectors included in the isotopic analysis shows typical isotopic fractionation from a hypothetical nitrate sample with an initial ratio of $\delta^{15}N$ = +6‰ and $\delta^{18}O$ = -9‰ (figure 4). The denitrification vectors of 1:1 and 2:1 are roughly the range of linear slopes of the ratio of $\delta^{18}O/\delta^{15}N$ for samples that have undergone denitrification.

The mixing model shows that the contributions of nitrate across the low-flow low fertilizer input samples are mostly from the nitrification of ammonium in soils, ammonium in fertilizers, and ammonium in precipitation except for three samples. The three exceptions are Money Creek site 7 ($7) and Six Mile Creek site 6 (6mc6) which are located in the manure and septic waste box and the Evergreen Lake deep-water near-dam sample (pSDA) which is located approximately on the line of separation between the soil ammonium source box and the manure and septic waste box. The two points along the creeks that reside in the manure and septic waste source box are the same samples which had their respective watershed's highest nitrate concentration.

The deepwater sample at Evergreen Lake sample on the mixing model is that it is the only datapoint from Evergreen Lake that is not in the vicinity of the other Evergreen Lake

samples. Another thing to note is that the near dam sample is of course at the terminus of the lake just before reaching the dam which also means that it had spent the longest time in residence than the rest of the lake water. Additionally, denitrification is an anerobic microbial process that takes place under reducing conditions, essentially when the water column is anoxic. The deepwater Evergreen Lake data shows that the conditions at the time of sampling were indeed anoxic which can suggest that denitrification is likely to occur. The next closest Evergreen Lake data point on the isotopic mixing model to the deep near dam sample was the location 1 deep sample (deep-1), which was the sample taken below the photic zone (i.e. where photosynthesis occurs and dissolved oxygen concentration increase during the day time) at a depth of greater than 3 meters. However, the dissolved oxygen concentration of the Evergreen Lake deep-1 sample was measured at 9.44 mg/L which is indeed oxic conditions under which denitrification likely will not occur. The comparison of the isotopic ratios of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ between deep-1 and the deep near dam sample shows that the deep near dam sample had a relative enrichment of both constituents of nitrate, which could be indicating a detectable amount of denitrification occurring between those two points.

While this isotopic mixing model does display results as sources it is indeed a mixing model which shows how things have evolved from their source. That being said where the datapoints plot on the $\delta^{15}N_{NO3}$ vs $\delta^{18}O_{NO3}$ mixing model is not necessarily the true source of each datapoint as isotopic fractionation may have altered the isotopic ratios of that sample of which the mixing model displays the end-member. Because of this aspect of the mixing model and the nature of stable isotopic ratio analysis this method is very open to interpretation, and in our case more so as we have a limited dataset due to budgeting and the extremely low concentration of nitrate that were captured during this sampling event.

The isotopic analysis of $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ of nitrate for our autumn season sample set indicate that fertilizer is not likely a major principal contributor to the nitrate nitrogen found in Lake Bloomington for the low-flow autumn season. The isotopic analysis points in the direction of nitrification of ammonium fertilizers and from soils as being the most frequent contributors and manure and septic waste having the highest magnitude contribution to the nitrate that is found not only in Lake Bloomington but also Evergreen Lake. Overall, these two watersheds are virtually identical in their water chemistry for the baseflow autumn sampling. This dataset is likely too small at the current time to fully assess the roll of denitrification, but it can be done with a complete dataset that captures high-flow stream conditions in spring when fertilizer inputs would be higher. Additionally, the addition of a spring time high-flow conditions sampling will greatly improve the determination of nitrate sourcing across these watersheds.

CHAPTER V: CONCLUSION

Analysis of major ions in the trilinear piper diagram shows that there is no major difference in general ionic composition between the watersheds and both the lakes and streams share calcium-magnesium bicarbonate type waters which further solidifies the extreme similarity between these two watersheds. Not only are the watersheds similar in terms of their geography, geology, and land use but there is a direct similarity in terms of the water type, which is logical as water type or hydrofacie is primarily controlled by the geology and land use of an area. Major groundwater interaction does not appear be taking place during these baseflow conditions. However, to fully determine the extent or lack of groundwater interaction, it is necessary to take shallow groundwater samples from across the study area in tandem with collection of samples from the streams and lakes.

The results of the dual nitrate isotope analysis suggests that nitrate fertilizers and atmospheric deposition of nitrate are not the principal contributors to the nitrate that is found in Lake Bloomington for autumn baseflow conditions. Instead, the mixing model suggests that the nitrate was most likely sourced from the nitrification of ammonium in precipitation and in the soil or from upstream sources of manure or septic sewage. Based on the results of this sampling it appears that the bulk of the nitrate in the lakes is coming from upstream locations as opposed to from groundwater during this period. The combination of the isotopic analysis with the concentrations of nitrate suggests that for this low-flow/baseflow autumn sampling, the only abnormal contributors of nitrate are manure and/or septic waste that was seen on those two final stream locations. Additionally, the isotopic ratios in tandem with the measured parameter of dissolved oxygen suggest that for Evergreen Lake in the deepest portion of the lake near the dam, denitrification had likely occurred. For Lake Bloomington the measured dissolved oxygen

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concentrations were all well outside the bounds of hypoxic or anoxic conditions which is a strong indication that denitrification was not occurring at that time. This suggests that the contributions of nitrate nitrogen in both watersheds were very similar, with the main difference between the lakes being that denitrification was taking place in Evergreen Lake but not in Lake Bloomington. Since this study only had data for one sampling event, definitive deductions cannot be made for why Lake Bloomington experiences frequent and near annual nitrate nitrogen exceedance when Evergreen Lake does not. However, at this time of the year in autumn, it appears the watershed contributions are nearly identical whereas the processing of nitrogen between the two lakes is not identical. As this sample set is quite limited in both its size and by the low nitrate concentrations captured during these low flow conditions, more frequent sampling and data will be needed to do a multi-year seasonal study to determine why Lake Bloomington whether there are different sources of nitrogen between the two watersheds.

It is recommended that more detailed investigation on municipal sewage systems and residential septic systems take place to ensure that all systems are operating in an acceptable fashion and not leaking, overflowing, or in a deteriorating state. It is also recommended that a more consistent investigation on the matter of nitrate exceedance on Lake Bloomington takes place throughout the future. There is also potentially something to be studied about the effectiveness of the de-stratifying aeration systems that are currently being used on both lakes as some of the data in this study suggests that the destratification system may be reducing effects of denitrification by keeping the water columns oxygenated.

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