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Nitrate Contamination and Nitrogen Isotope Compositions in the Bazile Groundwater

Management Area– A Water Quality Study. Creighton, NE

An Undergraduate Thesis Proposal

By

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Presented to

The Environmental Studies Program at the University of Nebraska-Lincoln

In Partial Fulfillment of Requirements

For the Degree of Bachelor of Science/Arts

Major: Environmental Studies

Emphasis Area: Natural Resources

Thesis Advisor: Troy E. Gilmore

Thesis Reader: Galen I. Richards

Lincoln, Nebraska

1 May 2019

ABSTRACT

Surface water nitrogen contamination is a pervasive issue in Nebraska, and agricultural practices are the main source of nitrogen input to streams (Spalding and Exner, 1993). Nitrate can come from inorganic fertilizers such as anhydrous ammonia, or animal waste. Studies have been conducted on nitrates dating back to 1947 (Addleman, 1985). The Bazile Groundwater Management Area (BGMA) located in northeast Nebraska has historically had high nitrate contamination. This qualitative study assesses the seasonal sources of nitrogen to stream water. It is predicted that the source of input is from commercial synthetic fertilizers. By using nitrogen-oxygen isotope methods, the source of nitrogen input to streams can be determined by isotopic ratios. 14 nitrogen-oxygen isotope samples were taken at 7 different locations in the BGMA during fall and winter to assess the seasonal variability of nitrogen pollution. Results showed that in the fall, nitrate was being derived from a mixture of anhydrous ammonia and manure, whereas in the winter the source of nitrate was primarily anhydrous ammonia. Nitrate contamination levels were also recorded at each site location and most were found to be above 10 mg/L. When 88% of rural Nebraskans utilize groundwater for drinking water (Nebraska Groundwater Quality Report, 2017), it is important to know how much nitrate is entering streams, and where the nitrate is coming from.

INTRODUCTION

The hydrologic cycle describes the continuous circulation of water and moisture on the Earth. Precipitation is the source of most all freshwater resources. Rain falls nearly everywhere but its intensity varies spatially. This water infiltrates the soil or contributes directly to rivers and streams as runoff (Briggs et al., 1972). Similarly, evaporation and transpiration occur everywhere, but the degree at which this occurs depends heavily on climactic conditions. Most precipitation occurring inland never reaches the ocean due to the hydrologic cycle. Movement of water on land and in the atmosphere is easy to understand because its changes can be observed (Winter, Harvey, Franke, Alley, 1998). Groundwater is a water resource involved in the hydrologic cycle below the surface, and it is defined as the water that occurs in open spaces below the ground (Winter, Harvey, Franke, Alley, 1998). Groundwater fills the pores spaces of geologic material like silt, sand, gravel, sandstone, and limestone. These geologic units bearing water are called aquifers, which can be used to yield water for human use.

There are many large groundwater aquifers throughout the United States. Nebraska in particular is comprised of several different aquifers that make up the High Plains Aquifer/Ogallala Aquifer. This aquifer extends from South Dakota to Texas. Two-thirds of the groundwater in this aquifer is in Nebraska (Gurdak, 2009). The depth to water table levels vary significantly across the state. In some areas, the volume of groundwater available for human use expands over a few gallons per minute to hundreds to thousands of gallons per minute. Figure 1 indicates the generalized depth to groundwater table in Nebraska. Northeast counties, most notably, in the Pierce, Antelope, and Knox counties, the depth to water table is shallow at less than 200 feet below the land surface and half is considered to be less than 100 feet deep. Shallow aquifers are more likely than deeper ones to initially suffer from contamination problems (Gao et

al., 2012). The depth to groundwater is shallowest in the stream valleys of Bazile Creek (NRD Data, 2016).

Table 1. Depth to groundwater table in Nebraska

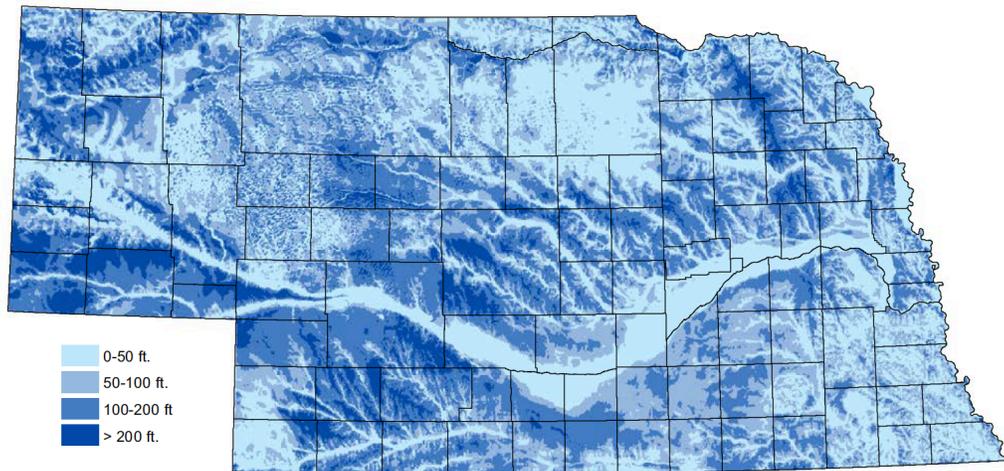


Figure 1. Generalized depth to groundwater in Nebraska. Depth is determined in feet. Dark blue corresponds to deeper depths in the aquifer. (Source: University of Nebraska, Conservation and Survey Division, 1998)

Nebraska is a rural state, comprised mainly of farms and small towns. 88% of Nebraskans rely on groundwater for their source of drinking water (Nebraska Groundwater Quality Report, 2017). This water resource is also used by the agricultural industry for the purpose of crop irrigation. In 2014, the USDA quantified 3.4 million hectares of land relies on groundwater for irrigation methods (USDA, 2014), (Spalding, 2000) west to east in low to high gradients. This in turn characterizes land use practices across the state (Wilhelmi, 2000). Roughly one-third of land in Nebraska is irrigated, and it is concentrated in the northeast (Gurdak, 2009). Figure 2 indicates the intensity at which irrigation practices are used. Northeast Nebraska is primarily composed of center irrigation pivots. The application of large amounts of nitrogen fertilizers

in regions of intensive agriculture, found in the state of Nebraska, contributes to excessive nitrogen in soils and excessive leaching into groundwater reservoirs. Extensive irrigation and use of synthetic nitrogen fertilizers together result in low N-use efficiency and high N loss (Gao et al., 2012). Several studies have also reported increasing incidence of nitrogen pollution and increases in the nitrogen concentration in the groundwater of regions where intensive farming is practiced (Hu, 2005).

Table 2. Irrigation methods practiced in Nebraska

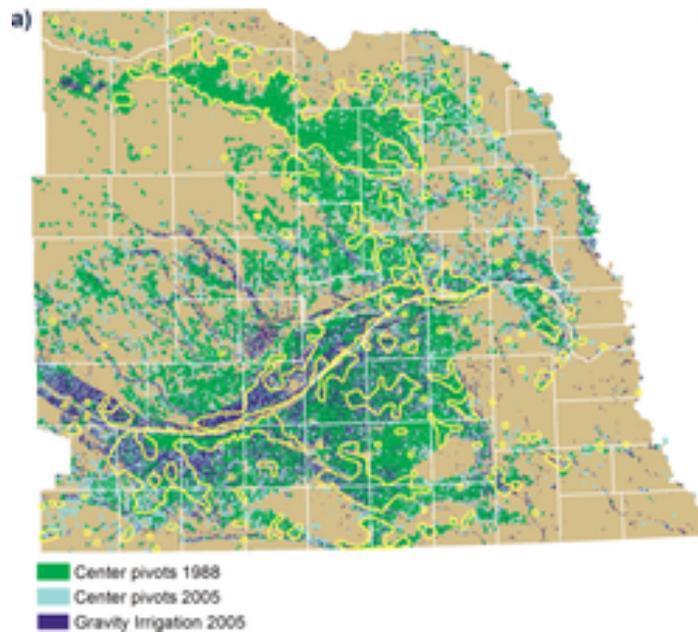


Figure 2. Center pivots are the most common practice used in Northeast Nebraska as indicated from data collected from 1988 and 2005. (Source Exner et al., 2014)

Certain parts of the aquifer in Nebraska are densely contaminated with nitrate. While fertilizers and manures are major input sources, nitrate also is formed from decaying plants and other organic residues (Gao et al., 2012). Northeast Nebraska is a region of the state that has historically had high nitrate contamination. Nitrate contamination has long been an issue in Nebraska, and has been studied intensely as early as 1947 in regions across the state (Addleman et al., 1985). Nitrate is a byproduct of agricultural production. Nitrate, once in the soil is water soluble and are easily transported through soil layers and eventually deposited into groundwater (Sahoo, Kim, Powell, 2016). Nitrate is the most common chemical contaminant in Nebraska groundwater resources that are connected hydraulically to agricultural fields (Spalding et. al, 2001). This is a problem because Nebraska’s groundwater resources are important and provide for over 95% of the rural population (NEDEQ, 2012). Figure 3 indicates that nitrate concentrations are highest in the eastern part of the state.

Table 3. Nitrate-N concentrations in eastern Nebraska

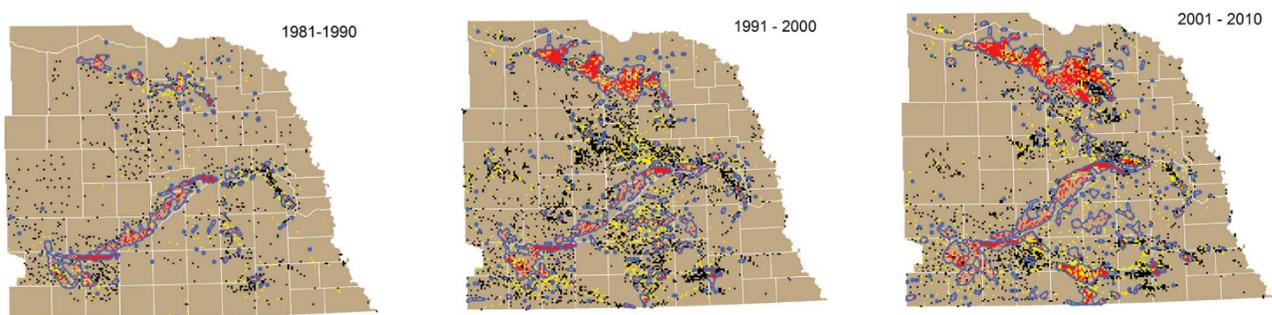


Figure 3. Nitrate contamination is concentrated in eastern Nebraska. Black cells depict average concentrations <5 mg N/L, yellow cells 5 to <10 mg N/L, and red cells 10 mg N/L. (Source Exner et al., 2014)

The high density of agriculture in northeast Nebraska is likely the cause of the nitrate pollution. Nitrates may occur naturally in groundwater systems, but generally they are a result of two sources of agriculture by (1) extensive use of synthetic commercial fertilizers for crops particularly in irrigated fields (Power, 1989), and (2) animal waste products from cattle (Eghball, 2002).

Anthropogenic inputs of nitrogen from agriculture impacts the health of aquatic ecosystems and creates risks for those who rely on domestic wells for drinking water. Nitrate exported into streams contributes to increased levels of nutrients, causing eutrophication. This in turn can adversely affect biodiversity and pose a risk to fish populations by reducing the amount of available oxygen in the water (Naugler, 2007). Excessive consumption of nitrate loaded water with concentrations of 10mg/L NO₃ or higher has been linked to methemoglobinemia or 'blue baby syndrome' in humans (Weisenburger, 1991) and (Mueller, 1996), stomach cancer, and nitrate poisoning (Zápata, et al., 2014) and hypertension, goiter, stomach cancer, thyroid disorder, cytogenetic defects, and birth defects (Sahoo, Kim, Powell, 2016).

The use of synthetic commercial fertilizers, such as anhydrous ammonia, are widely used in part because plants in the family Poaceae such as corn (*Zea mays* L.), are unable to fix nitrogen. Corn cannot use organic forms of nitrogen, such as found in the atmosphere (diatomic nitrogen, N₂) (Galloway, 2004). Corn must undergo a process called mineralization in order to transform organic nitrogen into a plant available nitrogen nutrient, nitrate. On large-scale crop production fields, there is not enough naturally occurring nitrate available to sustain growth, so farmers must apply synthetic fertilizers to overcome this shortcoming. Often times farmers over-apply fertilizers, which results with large quantities of waste, nutrient leaching, and runoff (Liang and MacKenzie, 1994).

Intensive livestock farming is one of the main causes of nitrate contamination in groundwater, in which large numbers of cows, pigs, or chickens are housed together in a small area. Demand in livestock production has increased dramatically, resulting in more waste products per farm (Sahoo, Kim, Powell, 2016). Livestock waste contains both inorganic and organic forms of nitrogen. The inorganic fraction is equivalent to nitrogen emitted in urine and usually greater than the organic one. Microbial degradation decomposes waste that contains organic nitrogen through denitrification, changing nitrogen to ammonia, then ammonia to nitrite, then nitrite easily oxidizes to nitrate (Sahoo, Kim, Powell, 2016). Given the nature of the breakdown of nitrogen containing compounds to nitrates, improper management of livestock waste can present serious threats to groundwater. Pollution input pathways include surface runoff from farm buildings, improper discharge, leaking from a storage facility, and excessive land application of wastes (Sahoo, Kim, Powell, 2016). Animal waste management is important to monitor for the conservation of groundwater, and for human health.

According to mass balances, less than 30% of anthropogenic nitrogen input into watersheds are exported to the oceans from surface water and streams. This means that 70% of nitrogen loads are either volatilized, denitrified, or stored in watersheds and aquifers. Due to the spatial and temporal importance of nitrogen retention and bioactivity it can be difficult to accurately quantify the input source at a watershed scale (Mayer et. al, 2002). However, nitrogen from animal waste or commercial fertilizers have different isotopic compositions (Meija, 2016). The ratio of $^{15}\text{N}/^{14}\text{N}$ nitrogen isotope compared to the $^{18}\text{O}/^{16}\text{O}$ oxygen isotopes in isotope analysis gives useful information about the input (Mayer, et al., 2002). Generally speaking, isotope application in hydrology is used to obtain knowledge about conservative tracers of ground water flow paths, identification of source regions in watersheds, estimation of residence

times of subsurface fluids, estimation of flow rates, identification of aquifer recharge areas, estimation of solute exchange among phases in systems, determination of extent of chemical reactions in subsurface and calibration of flow models (Sidle, 1997).

Knowledge of the quality of the Nation's water resources is important because of the implications to human and aquatic health, and because of the significant costs associated with decisions involving land and water management, conservation, and regulation (Bruce et al., 2003). This research will be conducted in order to learn more about the source of nitrogen inputs into streams in a highly agricultural area. The generation of this knowledge will produce new studies based on the nitrogen-oxygen isotope data that is collected. This paper will discuss nitrate concentrations collected in northeast Nebraska and will conduct $^{15}\text{N}/^{18}\text{O}$ isotope analysis in order to determine the input source.

PAST RESEARCH

Few studies have been conducted in the Bazile Creek Watershed. Most recent research is discussed in detail. 117 irrigation wells and 8 domestic wells were sampled in the Bazile Creek study area. The focus of this study was to collect nitrate contamination and water quality measurements in the Ogallala group or the Plio-Pleistocene sand and gravel aquifer units (Gosselin, 1991).

A study conducted in 2000 researched the agrichemical contaminants near Creighton, NE. A nitrogen-oxygen isotope analysis revealed that the source is primarily from synthetic commercial fertilizers. Furthermore, based on groundwater flow paths it was predicted that nearby private wells would be impacted in 20 years by the nitrate contaminant plume (UNL, 2000). A contaminant plume is an underground pattern of a densely contaminated pollution

source created by the movement of groundwater, with the contaminants spreading in the direction of groundwater movement. Groundwater follows flow paths throughout the aquifer, and because private wells are situated in the flow path it is suspected that citizens may be impacted by the contamination. However, there are a variety of different discharge locations throughout the creek where the contaminant plume may disperse and exit the groundwater system (UNL, 2000).

Lastly, an EPA-funded study was conducted to evaluate water quality in the East Branch Verdigris Creek (EBVC) watershed in 2005. Results from this study indicate that groundwater in this region is highly contaminated and stakeholders of this area (citizens, government, businesses, and the city of Creighton) are concerned about the high concentration of nitrogen, phosphorous, and sedimentation occurring in surface water originating from groundwater discharging into streams (UENRD, 2005).

It is important to research nitrate contamination because nitrate pollution has become a pervasive problem in the United States. Quantitative research is essential in determining the source input and necessary changes to management strategies. In areas where several sources may be the culprit of contamination, measuring contributions of different sources of nitrate loads greatly facilitates the understanding of anthropogenically-derived groundwater contamination (Kellman and Marcel, 2001).

Past research in the area assessed groundwater quality by sampling irrigation and municipal wells for nitrate concentrations as well as conducting water quality research in the area focusing both on surface water and groundwater. The nature of this research is qualitative and requires numeric data collection. The research design was created in an effort to learn more about the Bazile Creek Watershed and to gain an understanding of variability in stream water

nitrate concentrations and sources throughout the course of the year by taking nitrogen-oxygen isotope samples seasonally. The high susceptibility of the region to nitrate contamination gives further purpose to research by determining the methods by which nitrates enter surface water streams.

STUDY SITE DESCRIPTION

Bazile Creek is a watershed located in northeast Nebraska and encompasses a major agricultural region. Nitrate contamination problems in surface waters have been well documented in the large watershed because the application to cropped fields of both mineral nitrogen and cow manure is a common practice (Kellman, 2003). This study was conducted within the Upper Elkhorn, Lower Elkhorn, Lower Niobrara, and Lewis and Clark NRDs. The study area consists of three distinct topographic regions. (1) The plains, (2) rolling hills, and (3) dissected plains. This area is comprised of stream deposited silt, clay, sand, and gravel covered by loess or wind deposited silt. There are a variety of different soil characteristics across the region (Gosselin, 1991). However, most soils in this region are well drained and are absorbent to precipitation. The land has a high permeable unsaturated zone with a high density of irrigation pivots (Snow and Miller, 2018). The land elevation ranges from about 1,450 to 2,100 feet above mean sea level. The climate in this area is typical of interior mid-latitude continents. Land use in this region is dominated by agriculture practices with a total of 90-95% across the entire area (Exner et al., 2014). The most used fertilizer input is anhydrous ammonia (Gosselin, 1991). Figure 4 shows the Bazile Creek Management Area highlighted in Northeast Nebraska.

Table 4. Bazile Creek Management Area.

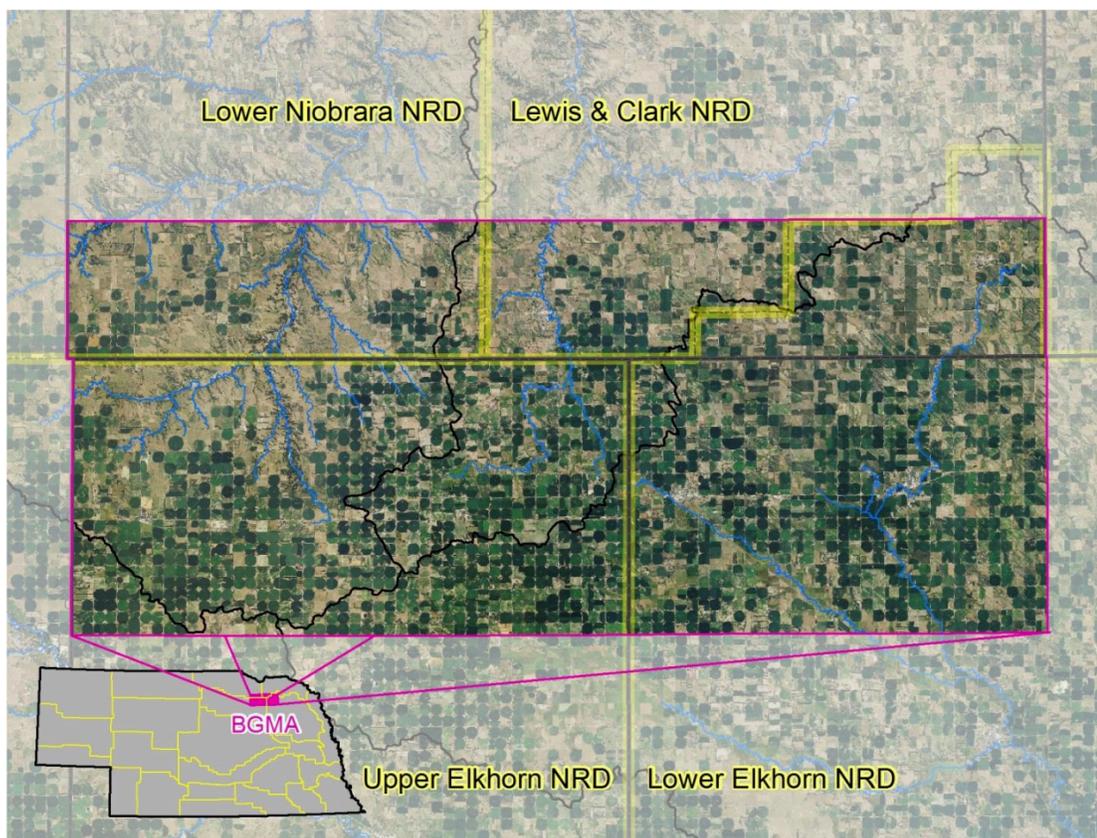
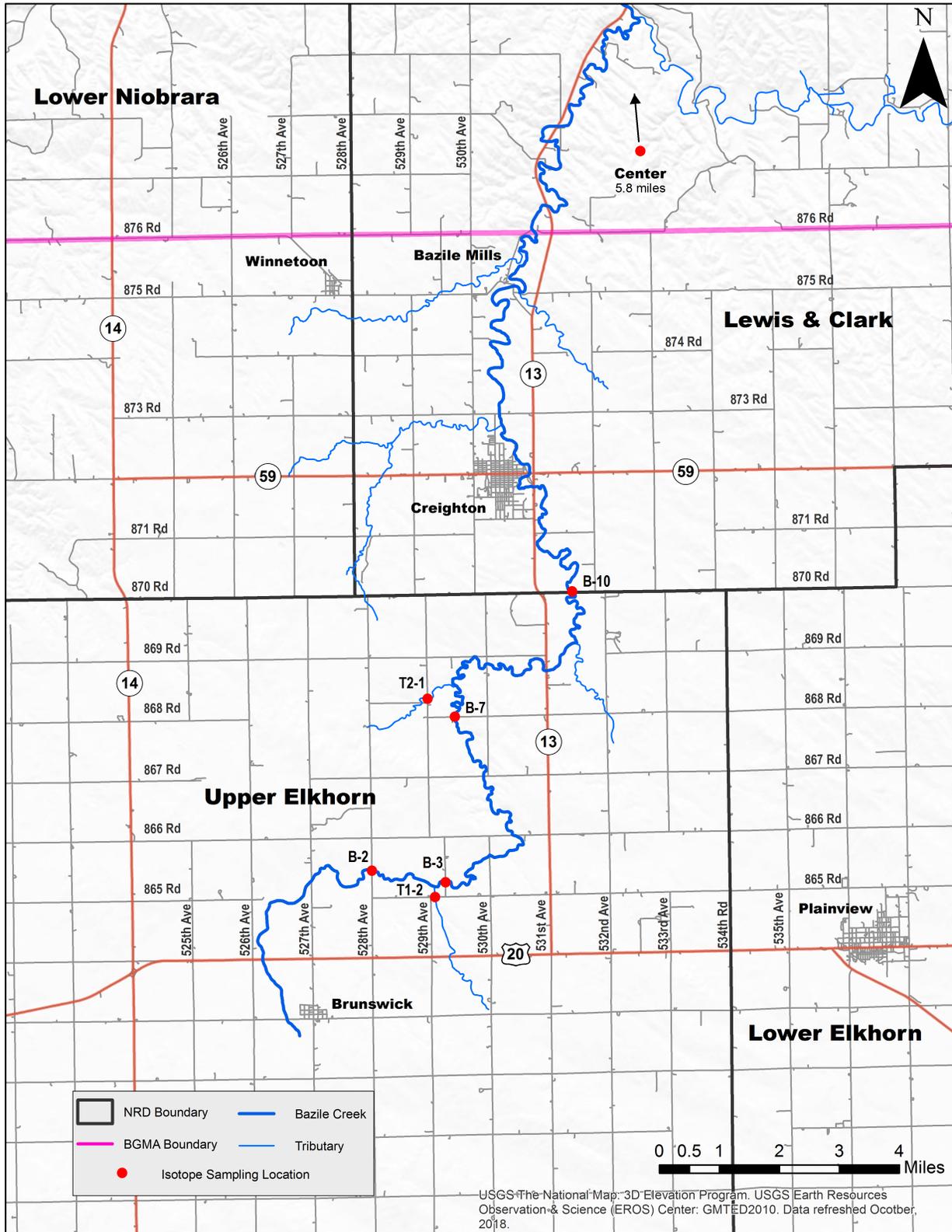


Figure 4. Included in the BGMA are the Upper Elkhorn NRD, Lower Elkhorn NRD, Lewis and Clark NRD, and the Lower Niobrara NRD. Source: Bazile Groundwater Management Area Plan, NE DEQ and NRD Report, 2016.

METHODS AND SAMPLE COLLECTION

In total, 14 surface water nitrogen-oxygen isotope samples were collected from seven surface water sampling sites along Bazile Creek and tributaries in the Bazile Creek Management Area. Each of the surface water isotope samples were also analyzed for nitrate concentration. Geography of each site includes large streams and narrow tributaries. Each sample was collected at sites along an 18 mile reach, chosen by the Upper Elkhorn NRD and lead scientist Troy Gilmore. Sites were selected to characterize major discharge locations and tributaries. The site names were Center, B-10, T2-1, B7, B3, T1-2, and B-2, where the letter “B” corresponds to sampling taken place on Bazile Creek, the letter “T” correspond to tributaries off of Bazile Creek. A large reach is required to assess the differences in water quality and nitrate samples from each site. The map of the study site (figure 5) shows each location that is sampled for nitrogen-oxygen isotopes. The reach includes areas located in the Lower Niobrara, Lewis and Clark, and Upper Elkhorn NRDs.

Table 5. Map of sampling locations used in the field.



Data collected from each site creates a portfolio of characteristics which are then used by the Upper Elkhorn Natural Resources District. Water quality parameters were taken at each location in real time. These parameters included dissolved oxygen, temperature, pH, and conductivity for each sample. This provides data that indicates the quality of the surface water prior to sampling for isotopes. Certain chemical parameters change when the samples are stored so it is important to gather this information in real time with a multi-parameter probe.

NITROGEN-OXYGEN ISOTOPE FIELD SAMPLE PROTOCOLS

Samples were collected in 250mL polyethylene bottles. Surface water was sampled in the middle of the stream by inserting the plastic bottle a few inches under surface flow. When sampling on bridges, the samples were collected using a submersible Whale pump. The Whale pump brings up the sample from the stream. Potential contamination is avoided by washing the bottle and lid with sample water at least three times. When sampling with the pump, purging the tubing for at least a minute is required to reduce sample contamination. Water was collected freely, and filtering or acidifying the sample for preservation is unnecessary because samples were frozen less than 24 hours after collection. An inch of headspace at the top of the bottle was left and the lid was securely put back on. Site attributes such as time sampled, date, location, and sample collected for identification during sample analysis were recorded. When the sample was collected, the sample was put in a cooler on ice and to keep it under cool temperatures. The samples were then held over ice until transported to the Water Science Laboratory on the University of Nebraska-Lincoln campus in Lincoln, Nebraska. Once at the Water Sciences

Figure 5. The red points indicate locations where sampling took place. NRD boundaries are separated and Bazile Creek and tributaries are highlighted in blue. Created by Galen Richards, UNL Graduate Student, Natural Resources Department.

Laboratory the samples were frozen. Samples were thawed only immediately before isotopic and nitrate analysis.

NITROGEN-OXYGEN ISOTOPE ANALYSIS

Two instruments were used to assess the data after field collection. Nitrate samples were assessed using a Seal AQ2 Autoanalyzer in the Water Sciences Lab. The AQ2 provides rapid and precise colorimetric analysis of many water samples for parameters such as ammonia, nitrate, and phosphorus. Prior to analyzing the nitrogen-oxygen isotope data, the nitrate concentration of each surface water sample was determined so that they could be properly analyzed by the mass spectrometer. An Isoprime Dual Inlet Isotope Ratio Mass Spectrometer was used for $^{15}\text{N}/^{18}\text{O}$ isotope determination. The change in composition of isotopes happens in a predictable way due to physical laws (Snow and Miller, 2018). The isotope ratio mass spectrometer detects fractionations of nitrogen and oxygen isotopes. There are quality assurance and quality control measurements provided within the nitrate analysis, such as standards and blanks that ensure results are accurate. The quality of data should be 97-99% accurate.

Nitrogen-oxygen isotopic values are often used as a tool to understand sources of contamination in order to effectively manage groundwater quality (Pastén-Zapata et al., 2014). The isotopic composition of nitrogen and oxygen is an essential method in order to determine origin, but it can also provide insight about nitrogen transformation processes such as volatilization and denitrification (Roadcap, 2001). Samples that are collected in the field have a chance of being denitrified by bacteria before lab work begins, so it is important to freeze samples immediately after collection (Danielescu et. al, 2013). In field methods are important to reduce this type of error.

Many studies in the past have used nitrogen and oxygen isotope techniques in order to identify nitrogen sources and to chart nitrogen transformations in the groundwater (Aravena, Evans, and Cherry, 1993). This method is used widely as a determination of source input. Studies have used this method in Nebraska as well as in other geographical regions across the world (Hu, 2005).

More specifically, the $^{15}\text{N}/^{14}\text{N}$ nitrogen isotope ratio in nitrate can suggest the source of nitrogen input into groundwater and streams (Naugler, 2007). Generally, nitrate produced from synthetic commercial fertilizers, such as anhydrous ammonia, an atmospheric nitrogen source, have nitrogen isotope ratios of between -2 and +4 (per mil per thousand, ‰). Nitrate produced from animal waste or sources have nitrogen isotope ratios of greater than +9.0 ‰ (Bruce et al., 2003).

Table 6. Predicted nitrate source values in per mil per thousand, ‰

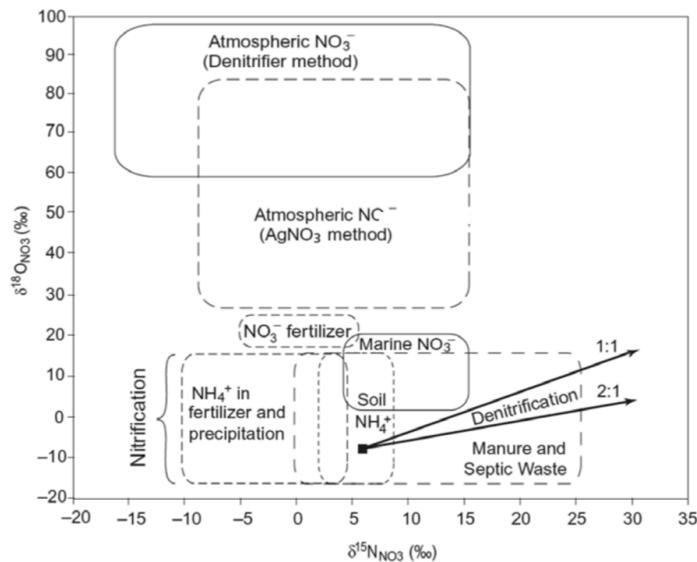


Figure 6 . Expected variation of $^{15}\text{N}-\text{NO}_3$ and $^{18}\text{O}-\text{NO}_3$ from a variety of sources, along with the predicted trends due to denitrification (Snow and Miller, 2018).

Figure 6. is a typical plot where nitrate isotopic studies have been conducted and found a reoccurring relationship between N-isotopes and O-isotopes. When all the samples have been collected, $\delta^{18}\text{O}$ (per mil, ‰) and $\delta^{15}\text{N}$ (‰) will plot in one of these areas on the graph. The nitrogen-oxygen isotope ratios suggesting denitrification are shown on the figure.

Sources of nitrate in groundwater can be classified in two distinct source characteristics, non-point and point sources. Non-point sources describe pollution that is untraceable to a single location. These sources are both indicative of agriculture practices and these occurrences impact citizens living in rural areas. There has been significant research conducted in order to determine the extent of groundwater nitrate contamination and the processes that can weaken nitrate levels in groundwater. It is essential to understand input sources in order to protect water quality and to reconcile the contributing source of the pollution. It is important to understand the local nitrate concentrations in order to assess potential impacts and further in understand hydraulic flow paths. (Kendall, 2000).

By analyzing the stable isotopes of nitrate in surface water, it helps determine the source of input to the stream. Compositions of nitrogen isotopes coupled with oxygen isotopes provide information about the processes occurring in the stream. This research will provide needed information for the Upper Elkhorn Natural Resources District that will then be used to effectively manage agriculture practices and understand the source of nitrate input into the streams in the BGMA.

RESULTS

Water quality parameters were measured using a multi-parameter probe and they were temperature, pH, dissolved oxygen (DO), and specific conductivity (SPC). There was little variability in fall water quality parameters across the 7 locations. Surface water temperatures

ranged from 10.78°C at Center to 8.93°C at B-2. The pH values are all similar with neutral to slightly alkaline values, which is common of most surface water. It was important to collect samples on the same day because changes in stream characteristics can happen daily, if not hourly.. In winter, temperatures varied from 0.35°C at Center to 6.42°C at T1-2. The pH increased slightly increased in most locations or stayed relatively the same at a pH of 8.

The nitrate concentrations collected in the fall at the 7 locations range from low to high concentrations. Location T2-1 had the lowest nitrate concentration at 3.576 mg/L. Locations with values under the recommended drinking water limit are B-2, B-10, and Center. The highest fall nitrate concentration occurred at T1-2 at 16.1 mg/L. Other locations above 10 mg/L are B-3 and B7. The winter nitrate data shows an increase in nitrate concentration. The highest concentration recorded was at B-2 with a concentration of 21.465 mg/L. The lowest nitrate concentration was found at T2-1 at 8.07 mg/L. All other locations had nitrate concentrations above 10 mg/L.

The surface water isotopes were collected at all seven sample locations at the same time as water quality parameter collection. Fall $^{15}\text{N}/^{14}\text{N}$ nitrogen isotopes and $^{18}\text{O}/^{16}\text{O}$ oxygen isotopes found at each location can be seen in figure 11. The ratio of these isotopes indicates that the primary source of input is commercial fertilizer based on similar previous research conducted on isotope data in other areas (Mayer et al., 2002). The ranges collected correspond to fractionations found from fertilizer input. The range of values collected for ^{15}N composition for the 7 surface water sites were from $+4.74\pm 10.8\%$.

Table 7. Specific Conductivity in uS/cm.

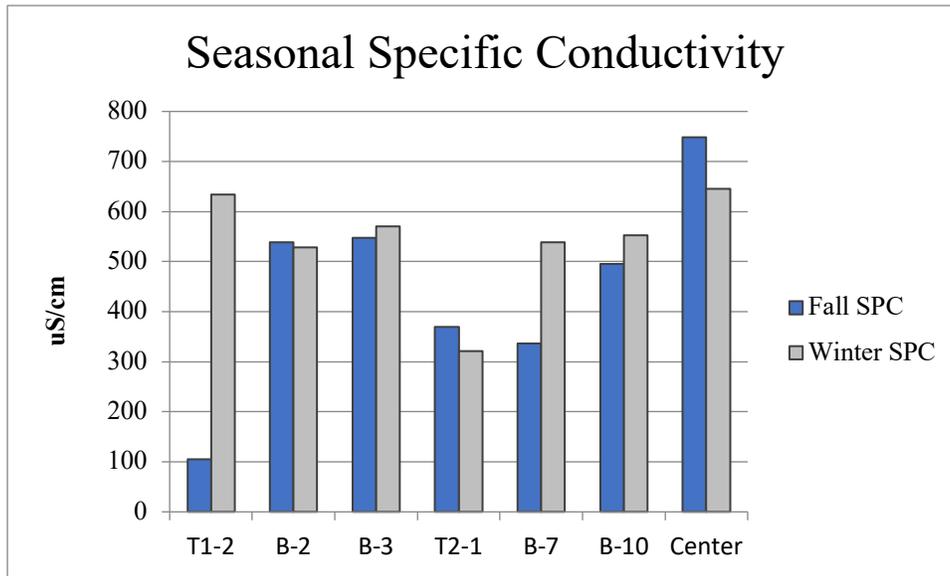


Table 7. Changes in specific conductivity from fall to winter in the BGMA.

Table 8. Nitrate concentrations in mg/L.

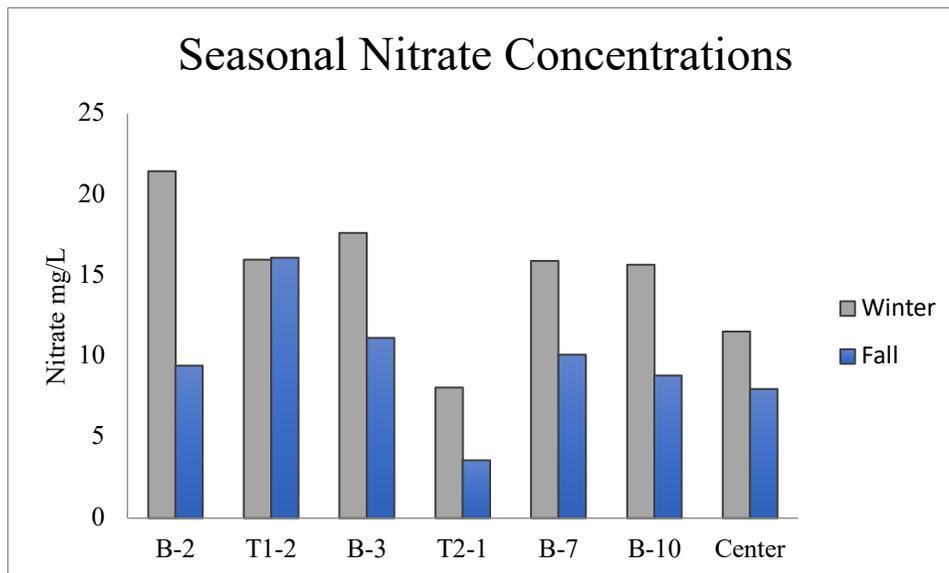


Figure 8. Seasonal nitrate concentrations at 7 locations along the BGMA. Taken in fall and winter.

Table 9. Water Quality Parameters in Fall.

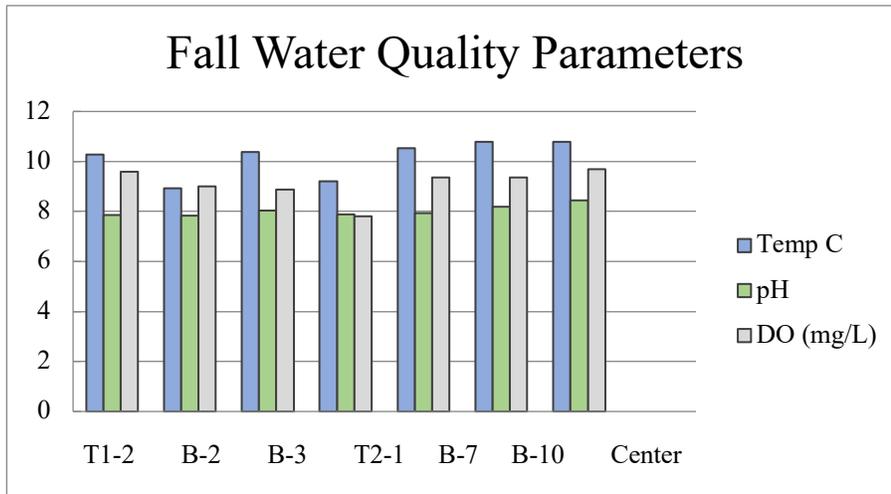


Figure 9. Different parameters measured in units indicated on the legend. Water quality parameters suggest health of stream.

Table 10. Water Quality Parameters in Winter.

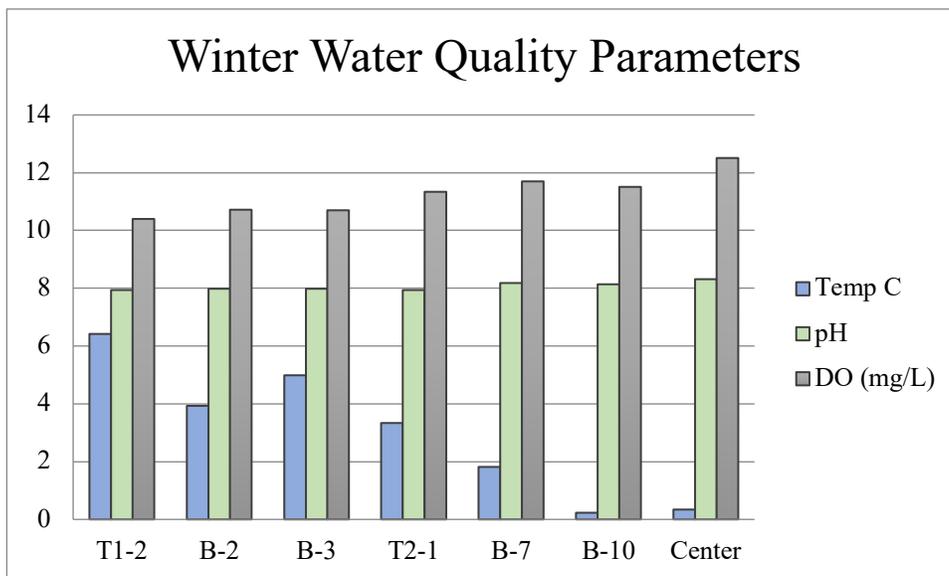


Figure 10. Different parameters measured in units indicated on the legend. Water quality parameters suggest health of stream.

Table 11. Nitrogen oxygen isotope values in the BGMA in ‰.

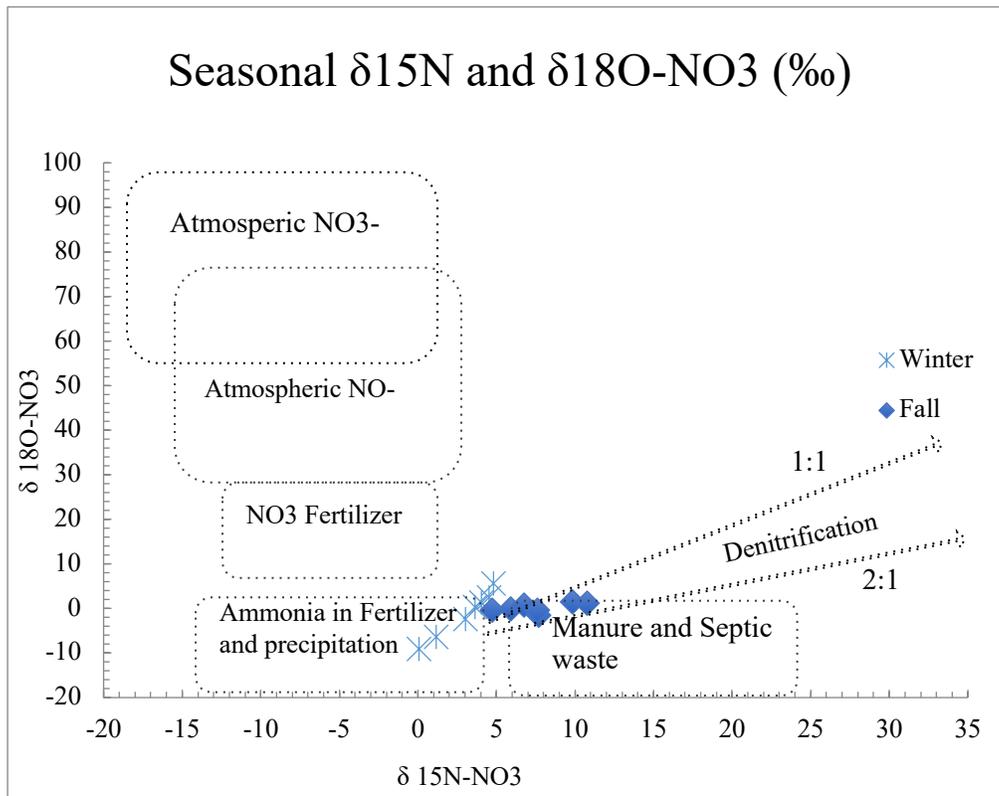


Figure 11. Seasonal nitrogen oxygen isotope values. Graph template used from Snow and Miller, 2018.

DISCUSSION

Fall and winter samples were taken on October 13, 2018 and January 26, 2019, respectively. Dissolved oxygen (DO) is an indicator of water quality. Average DO increased by 2.17mg/L from fall to winter. DO is used by aquatic life and is the constituent that determines the health of water (Perlman, 2017). Streams that have high stream flow velocities have higher DO values whereas stagnant water has lower values (Perlman, 2017). Seasonally, DO varies with temperature. In the spring and winter when temperatures are low, the DO concentrations are higher, and in the fall and summer when temperatures are high, the DO values are lower.

Samples were collected in the fall and the winter, and as the temperatures dropped for the winter season, DO changed accordingly. Specific conductivity (SPC) is the measurement of dissolved ions present in water. The more ions present in water, the more efficient water becomes as a conductor. Ions originate from the breakdown of solid compounds such as chloride, nitrate, sulfate, calcium etc., therefore SPC is a good indicator of water pollution (Murphy, 2007).

The pH levels of the streams stayed relatively the same as most were near neutral or slightly alkaline. Temperature decreased with atmospheric temperatures. Water temperatures taken at the seven locations are good indicators of groundwater fed streams or surface water fed streams. Temperatures recorded in the fall were similar ranging from 8-10 degrees centigrade. Air temperature influences stream temperature. In the winter, temperatures are more diverse ranging from a little above 0 to 6 degrees centigrade. The streams at locations B-7, B-10, and at Center had values of 1.82, 0.24, and 0.35 degrees centigrade. It is postulated that these streams are predominantly surface water fed. The temperature at these locations was -10°C on January 26th, and because the streams are colder than that of other locations, this suggests that since water has a low latent heat, it fluctuates slowly with air temperature.

The surface water streams are not used as a source of drinking water, however using the standard nitrate drinking water limit of 10 mg/L is useful as a reference in understanding the degree at which the streams are contaminated. Concentrations under 10 mg/L nitrate-N indicate lower contamination, or, safer water. The fall nitrate-N concentrations on average are lower than the winter nitrates. More of the locations had nitrate concentrations below 10 mg/L in the fall than in the winter. The winter nitrate concentrations were higher than in the fall and averaged 15.18 mg/L. The highest concentration occurred at B-2 of 21.465 mg/L. The fall nitrate concentration for B-2 was 9.427 mg/L. T1-2 remained the same with a concentration of 16 mg/L

in both seasons whereas the other locations all increased. Reasons pertaining to the increase of nitrates could be because of lowered surface water flow in the winter. Having lower surface water flow will increase the concentration of nitrates in the stream (Exner-Kittridge, et al., 2016). Denitrification is a process that removes nitrates from streams. Nitrate concentrations could have been higher in the winter as a result of less denitrification occurring in the winter months.

Nitrogen-oxygen isotope values for the fall show that the source is distributed between ammonium fertilizer and manure/septic waste. It is highly likely that there is mixing occurring between the sources, however it is suggested that the nitrates are primarily fertilizer derived with trace amounts of manure and septic waste that impacts the data. With trace amounts of manure and septic waste it can skew the results slightly to the right as the data indicates. Surface water with nitrate contamination can be a result of surface water runoff. Since subsurface flow and groundwater mixing was not accounted for, results cannot state whether nitrogen-oxygen isotope values come solely from surface water runoff. Mixing with nitrate-contaminated groundwater could possibly alter the input of nitrates to the stream. For example, if anhydrous ammonia was the primary input and the application leached into the groundwater system and recharged into the stream at a later date, flow paths cannot be differentiated by the isotope data. The nitrogen-oxygen isotope values in the winter also plot similarly in that the primary source suggests it is also from anhydrous ammonia. There are less values that suggest inputs of manure and septic waste with this data set. There are also a variety of reasons that the amount of manure or septic waste could have been reduced. Below freezing temperatures could have frozen manure on pastures, keeping the nitrogen from leaching or contributing to surface run off. Additionally, while the protocol for determining nitrogen-oxygen isotopes does not differentiate between manure and septic waste, the likelihood of organic nitrogen from private septic tanks on

homeowner's property from being a source of contaminant input as a result from leaking or pollution is less than the impact of manure input. Since the composition of nitrogen-oxygen isotopes decreased in both ^{15}N and ^{18}O , there is more data suggesting that the source is ammonium fertilizer than manure or septic waste. The streams are all located in pastures some distance away from private homes, therefore the source of input by human septic waste tanks is likely low.

14 nitrogen-oxygen isotope samples were taken along a large watershed during two seasons. There is some sample overlap indicated in results obtained which indicates that there is uniform input sourcing from all 7 locations. ^{18}O composition for the 7 surface water sites range from $-.371 \pm 1.39\%$. Although this data points to the primary source being inorganic fertilizers, more nitrogen-oxygen isotope samples should be collected during different seasons in order to have a more complete picture of nitrate sources to the Bazile Creek watershed. Taking nitrogen-oxygen isotope samples monthly or seasonally will create a better time series of input and can describe how water quality parameters and nitrate inputs change over time. The water quality parameters are useful in suggesting the health of the streams at given times. Water quality parameters can change hourly, so a constant method of data analysis would be insightful in determining true stream health.

Nitrate concentrations in the area were not taken from private wells, but instead from surface water streams. If nitrate concentrations are a concern in private drinking water wells, a separate analysis should be conducted by the homeowner or municipality. Only surface water samples were taken thus information pertaining to groundwater and groundwater mixing was not acquired. Future research endeavors should include both surface water nitrogen-oxygen isotope samples and groundwater nitrogen-oxygen isotopes taken seasonally. This is essential in

determining the amount nitrogen input with the potential surface water and groundwater mixing (Snow and Miller, 2018). Conducting a groundwater age dating analysis on groundwater discharging into the headwaters of Bazile Creek would be useful in understanding groundwater transit times and potential flow paths (Kendall, 1998). This would be particularly useful in determining the lifespan of a contaminant in the groundwater (Kendall, 1998). Additionally, a streambed sediment analysis could be useful in determining the potential of hydraulic conductivity in the stream. Understanding typical soil compositions in the area would be useful in determining how much nitrogen is leaching into the aquifer.

CONCLUSION

While the data obtained suggests the source of input is from inorganic fertilizers, there is potential for hydraulic mixing. Collecting nitrogen-oxygen isotope samples from more sites would be useful because other areas of the Bazile Creek Management Area could have different sources of nitrogen pollution. Water quality measurements indicate relatively neutral pH ranges. Some locations have high SPC values which indicate high concentrations of dissolved ions which can originate from pollution, precipitation, and dissolved minerals. Temperature is a good indicator of preliminary high groundwater recharge areas as higher surface water temperatures in the winter may indicate more groundwater recharge. Nitrate concentrations show an increase in winter as a potential result of lowered denitrification and less surface water flow. In conclusion, further research is needed in order to state definitive inferences, such as the source of nitrate input to streams, and assessment of water quality in the Bazile Creek Management Area.

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