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Nathan Roddy

University of Nebraska - Lincoln, nathan.rodny@huskers.unl.edu

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Isotopic and Geochemical Analysis of Nitrate Contaminated Groundwater in
Edgar, Nebraska

by

Nathan M. Roddy

A THESIS

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Under the Supervision of Professors David Loope and Daniel Snow

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Isotopic and Geochemical Analysis of Nitrate Contaminated Groundwater in Edgar, Nebraska

Nathan M. Roddy, M.S.

University of Nebraska, 2018

Advisors: David Loope and Daniel Snow

High nitrate concentrations in the groundwater beneath Edgar, Nebraska have been measured for well over a decade, exceeding the EPA's MCL of 10 mg-N/L. Investigating the isotopic signature of nitrate and groundwater have determined the likely source(s) of contamination. Apparent seasonal changes exist in nitrate concentration, isotope ratios, and geochemistry, suggesting that sources and flow paths change as a result of irrigation. Samples collected in December and May had very similar nitrate concentrations (average value of 13.7 mg-N/L) and isotopic ratios ($\delta^{15}\text{N}$ 4.46‰ and $\delta^{18}\text{O-NO}_3$ 20.21‰), suggesting synthetic nitrate fertilizers are the major source of nitrate in the groundwater. August samples, indicated other sources of nitrate present in the groundwater. Nitrate concentrations from the same sites increased to an average value of 14.65 mg-N/L and shifted isotope ratios of $\delta^{15}\text{N}$ to 9.30‰ and $\delta^{18}\text{O-NO}_3$ to 15.45‰. The changes are associated with proximity to irrigation and/or municipal wells. Shallow wells screened near the water table as well as deeper wells follow the same pattern of drastic changes in the August samples. Two wells located inside the city limits and more than a half mile away from any major well saw little to no change in nitrate concentration

or isotopic signature, indicating that they are unaffected by seasonal changes. Further evidence of mixing of waters can be seen with a subtle shift where water isotopes become more enriched in $\delta^{18}\text{O}$ -H₂O and more depleted in δD . Geochemistry supports an apparent mixing of waters.

Dedicated to my brother, Zach

He always supported me to peruse knowledge.
He pushed me to consider the reasons why I thought
and believed what I did.

You made me a better person and scientist.

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List of Abbreviations

<u>Abbreviation</u>	<u>Description</u>
‰	Per mil (1 in a 1000)
EPA	Environmental Protection Agency
GMWL	Global Meteoric Water Line
HCl	Hydrochloric Acid
H ₂ O	Water
K _d	Partition or Distribution Coefficient
LMWL	Local Meteoric Water Line
MCL	Maximum Contaminant Limit
N	Nitrogen
NDEQ	Nebraska Environmental Protection Agency
NDNR	Department of Natural Resources
NO ₃	Nitrate
NRD	Natural Resource District
SpC	Specific Conductance
UNL	University of Nebraska-Lincoln
USGS	United States Geological Survey
VSMOW	Vienna Standard Mean Ocean Water
WHPA	Well Head Protection Area
WSL	UNL Water Sciences Laboratory

Isotopic and Geochemical Analysis of Nitrate Contaminated Groundwater in Edgar, Nebraska

1.1 Introduction

Nitrate is one of the most common contaminants in ground water worldwide and exceeds national drinking standards in groundwater across the U.S. (Wassenaar, et al., 2006). Nitrate in Nebraska's groundwater is increasing in both concentration and areal extent (Exner et al., 2014). Nitrate in the unsaturated zones above much of the state's groundwater resources has not yet reached steady state (Exner et al., 2014). While recent changes in producer management practices have slowed increases in groundwater nitrate for some areas, irrigation and nutrient applications must be more effectively controlled to retain nitrate in the root zone. Nebraska's natural resource districts and many municipalities now wrestle with regulations designed to improve practices to reduce loading and minimize continued leaching of nitrate already stored in the vadose zone. To tackle these problems, more information is needed to better understand all aspects of the issue. Major causes of high nitrate found in groundwater include excessive fertilizer and irrigation use, over application of nitrogen from animal waste, abandoned feedlots and point source locations such as spills at manufacturing and storage sites.

The municipal drinking water nitrate maximum contaminant limit (MCL) set by the EPA for drinking water is 10 mg-N/L. Long term exposure to levels at or above the MCL of nitrate in drinking water are hazardous for all users, but they are especially dangerous for young children and the elderly.

The city of Edgar is located in Clay County in south-central Nebraska, and here as in most of the state, groundwater is a very important part of both life and the economy. As of July, 2018 Nebraska Department of Natural Resources (NDNR) Registered Well Database listed 3751 registered wells in Clay County, with the vast majority being irrigation wells. Many of the wells surrounding Edgar, including the public supply wells, have shown higher levels (~15-20 mg-N/L) of nitrate in the groundwater (Olsson Associates, 2011). In 2010, Edgar received funding from NDEQ to characterize the groundwater flow regime and to determine methods to respond to increasing nitrate concentrations within the Wellhead Protection Area (WHPA). The WHPA is defined as a 20-year transport of water supplying the municipal wells, taking into account property boundaries. WHPA maps typically have straight boundaries and corners. Even though a water parcel might only reach a small portion of a field, the entire field will be included so that farmers/property owners do not use special management practices for only small portion of the field.

The initial groundwater survey study conducted by Olsson & Associates provided background information on subsurface flow and the growing nitrate issue in the municipal wells (Olsson Associates, 2011). Olsson proposed four methods to circumvent or remediate the high nitrate in the groundwater: 1) construction of a new water treatment plant; 2) construction of a new well field outside of town; 3) development of a regional water supply system; and 4) construction of engineered wetlands and nitrate source extraction wells (Olsson Associates, 2011). They recommended the construction of a water treatment plant option because of the likelihood of consistent and long term reduction of nitrate and because it is the most cost effective option. A report by Spalding

and Jensen (2010) investigated the nitrate level in the vadose zone below Edgar, looking for various point and non-point sources where nitrate contamination is likely to have occurred. Spalding and Jensen (2010) discovered areas with higher nitrate concentrations that can be correlated to historical land-use.

The goal of my research is to determine the source(s) of nitrate present in the groundwater. To accomplish this goal, the investigation of nitrate isotope values (oxygen and nitrogen) were used to identify specific sources or processes that contribute or affect nitrate concentrations. Previous research has indicated that sources of nitrate can be characterized using stable isotope analysis (Gormly and Spalding, 1979) (Wassenaar, 1995) (Wassenaar et al., 2006) (Xue et al, 2009) (Minet, et al., 2017). The term “stable” denotes the isotope will not decay or degrade to form a different element under normal scenarios. The isotopic composition of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}\text{-NO}_3$ can help determine the source type(s) of the nitrogen (manure, fertilizer, or atmospheric). In addition, the analysis of groundwater isotopes ($\delta^{18}\text{O}\text{-H}_2\text{O}$ and δD (deuterium)) helps determine what part of the year (season) the water reached the aquifer based on local precipitation, as well as the possible mixing of different sources contributing to the groundwater.

Lastly, major ion composition (Na, K, Ca, Mg, Cl, SO_4 , and HCO_3) helps show whether water chemistry changes substantially different between contaminated and less contaminated zones, and helps evaluate regional sources of groundwater that are most prevalent in the WHPA.

2.1 Literature Review

2.1.1 Nitrate and Nitrogen

Nitrate is a very common substance found both naturally and artificially in groundwater. In high concentrations, nitrate can be harmful if consumed by humans; it has been linked to health effects such as methemoglobinemia and other reproductive and developmental issues (Fan & Steinberg, 1996). The EPA maximum contaminant level (MCL) is 10 mg- N-NO₃/L, though caution has been given to pregnant women, infants, and the elderly when level approach the limit, but have not reached the threshold. In agricultural areas, high nitrate in groundwater is usually caused by leaching from either crops receiving fertilizer or animal waste. Popular nitrogen fertilizers for much of the area include anhydrous ammonia (NH₃), ammonium nitrate ((NH₄)(NO₃)), and urea (CO(NH₂)₂). In many cases, ammonium nitrate and urea (UAN) are applied together as because urea is highly soluble and volatile. Once applied, it is rapidly hydrolyzed by urease enzymes in the soil and organic material, yielding two NH₄⁺ per each CO(NH₂)₂; it is then converted to NH₃ rather quickly (Rawluk et al., 2001). Ammonium nitrate on the other hand, though soluble in water, takes longer to dissolve and become available to plants. Isotopic analysis of the separate components (i.e. nitrogen and oxygen of nitrate) was used to determine the source(s) of nitrate in the groundwater in Edgar.

To better understand how nitrate behaves in water, a close look at the partitioning of nitrate is paramount. Once dissolved, nitrate travels as fast or faster than the water in which it is dissolved depending on the soil type (USEPA, 1999). This is because the partition or distribution coefficient (K_d) of nitrate, which is an estimate of the potential to

which a molecule adsorbs to a medium, is equal to that of water. As a result, nitrate will not sorb to the soil particles in any real capacity and will flow at the same rate as the rate. Due to a mechanism called anion exclusion, negatively charged ions such as nitrate (as well as other anions such as chloride and bromide) are able to concentrate at the wetting front water due to the charge imbalance present in soils with higher clay content (Sposito, 1984). Sand or silica (SiO_2) does not have a charge, whereas soils with clay tend to have a slight negative charge. Due to both the contaminant ion, in this case nitrate, and the clay rich soil having negative charges, the like charges repel one another. With the exception of very few locations where water is stagnant, this repulsion tends to be in the direction of flow, assuming no microbial interaction with nitrate is present in either the vadose or saturated zones.

The unsaturated zone below the root zone often has an active microbial community, where nutrients such as nitrate, phosphate, and sulfate are passing through, towards the water table. This active community of microbes consumes/respire nutrients such as nitrate and can ultimately change their form. This occurs when oxygen is in limited supply or absent and the next easiest oxygen bearing molecule for the microbes to use is nitrate. This specific respiration process is called denitrification, with the following conversion steps: nitrate (NO_3) to nitrite (NO_2) to nitric oxide (NO) to nitrous oxide (N_2O), and finally to nitrogen gas (N_2). If the environment is oxic rather than anoxic, bacteria can alter the nitrogen found in ammonium (NH_4) to form hydroxylamine (NH_2OH) to nitrite (NO_2) to nitrate (NO_3). (Francis, Beman, et al., 2007) Following the laws of thermodynamics, the process of denitrification, like many processes (if possible) use the least amount energy in order to complete the process. In this case, using less

energy would be preferentially using the lighter nitrogen and oxygen isotopes in nitrate to complete the process, resulting in an enrichment of “heavier” isotopes in the remaining water.

2.1.2 Isotopes

Isotope analysis became popular in the latter half of the 20th century due to improvements in technology and machining. Mass spectrometers became indispensable as tools for environmental investigations as differences in isotope abundances could be determined. The enrichment or depletion of a minor isotope, relative to a major isotope(s), could point to a particular process occurring. The notation used to display the relative enrichment or depletion of a minor isotope is the lower case Greek letter “delta” (δ). The unit used to express the relative abundance is per mil or ‰, which is one part per thousand parts. Equation 1 is used to calculate the relative ratio of two isotopes of an element.

$$\delta_{\text{sample}} = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) * 1000$$

Equation 1. This equation is used to calculate the relative depletion or enrichment of a minor isotope to the major isotope.

where is the enrichment/depletion of a minor (less abundant) isotope relative to the major (more abundant) isotope. In Equation 1, R_{sample} is the ratio of the minor to the major isotope in the sample. R_{standard} is the ratio of the minor to major isotope in an international standard. For nitrate, the R is $^{15}\text{N}/^{14}\text{N}$ or $^{18}\text{O}/^{16}\text{O}$ and is represented $\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}$ -

NO₃ respectively. For water the R is $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ and is represented $\delta^2\text{H-H}_2\text{O}$ or $\delta\text{D-H}_2\text{O}$ and $\delta^{18}\text{-H}_2\text{O}$ respectively.

Changes in isotopic composition can occur when reactions do not go to completion and/or when samples are collected improperly. This alteration is called fractionation, which is the partition of isotopes between two compounds contains the same element with different isotopic ration (Mariotti et al., 1981). Natural fractionation occurs constantly as a result of changes due to temperature changes (water freeze/thawing or evaporating) or metabolic processes. The vast majority of research has gone into studying the rates and conditions in which fractionation occurs. Fractionation can also be caused by samples not preserved correctly, for example, if the sample temperature reaches a point where the samples' molecular components (usually oxygen) begin to exchange with the atmospheric gases in the head space of the bottle or laboratory air. If a sample is not preserved properly (acid or freezing) microorganisms that are living in the sample can possibly metabolize the nutrient and artificially fractionate the sample further.

Differences in isotopic abundances due to natural fractionation have been used to study processes across many different fields of interest such as manufacturing, atmospheric, or biologic processes have allowed for the development of ranges along which isotopic abundances for a certain process will usually fall. For cases of nitrate contamination, these ranges can help determine if a single or multiple processes are responsible for the total contamination.

Nitrate

There are three sources of nitrate in the groundwater of the High Plains aquifer, synthetic fertilizers (created via Haber-Bosch process), biogenic fertilizers (manure and urea), and atmospheric sources (Gurdak et al., 2009). In their study Gurdak et al. (2009) indicate that on a whole, contamination of the High Plains aquifer comes from biogenic sources, in which ammonia is oxidized to form nitrate (nitrification). In some localized areas, however, in which other processes are occurring, such as denitrification. Generally, ammonia is added to fields in the form of anhydrous ammonia or ammonium nitrate fertilizer.

Much work has gone into the study of nitrate due to its abundant use in various forms as agricultural fertilizers. Beyond simply determining concentration, which in itself can be a powerful tool for locating point sources of contamination, looking at the isotopic composition of nitrogen and oxygen can more precisely determine the source(s) of contamination. For this data to be meaningful, research has been conducted to determine the isotopic ranges from many different nitrate sources including nitrate fertilizer, ammonia fertilizer, manure, sewage, denitrification, and naturally occurring nitrate from either the soil or atmosphere (Wassenaar, 1995).

Figure 1 is from Xue et al., (2009), who reviewed over one hundred and twenty other studies investigating the determination of nitrate by looking at $\delta^{15}\text{N-NO}_3$. By looking at all the different studies and their own reported isotope values, the authors were able to compile $\delta^{15}\text{N-NO}_3$ ranges from many known sources of nitrate. One thing the authors did not incorporate into this figure is denitrification, since it is not a source of nitrate, only a process that alters and masks the sources. Each of these sources have a

range of values that is generally agreed upon, but does have some slight variability.

Ammonium fertilizer, nitrate fertilizers, and urea are (in)organic fertilizers, which are produced by fixation of atmospheric N_2 and show small differences in $\delta^{15}N-NO_3$ content as a result of small fractionation during the subsequent processing of the fixed nitrogen (Flipse & Bonner, 1985). From Figure 1, we can see that these sources generally range from -5‰ to +5‰, which is within the normal range of atmospheric nitrogen deposition of -13‰ to +13‰ (Xue et al., 2009).

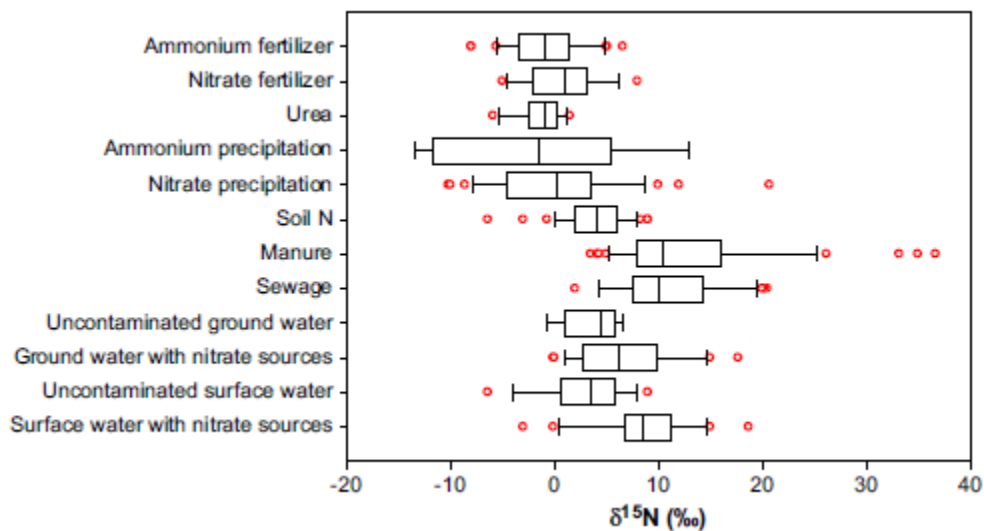


Figure 1. Box plots of $\delta^{15}N$ values of nitrate from various sources and sinks. Box plots illustrate the 25th, 50th and 75th percentiles; the whiskers indicate the 10th and 90th percentiles; and the circles represent outliers. Source: Xue et al. (2009)

Nitrogen in both manure and sewage is enriched with $\delta^{15}N-NO_3$ relative to other sources of nitrate due to the volatility of the ammonia (NH_3) during application causes a large enrichment of $\delta^{15}N-NO_3$ in the residual ammonium (NH_4^+) present in both sources. Wassenaar, (1995) and Girard & Hillaire-Marcel, (1997) report the range of sewer and animal waste to be +8‰-+16‰, but Widory et al., (2004) report typical values 10‰ -

20‰. Generally nitrate derived from manure and sewage will be the most enriched $\delta^{15}\text{N}$ - NO_3 in groundwater.

Use of $\delta^{18}\text{O}$ in nitrate analysis has become more popular in recent years due to its ability to refine different sources. Wassenaar (1995) suggested that $\delta^{18}\text{O}$ - NO_3 may be a good tracer of nitrate sources, because it distinguishes synthetic nitrate fertilizers from other nitrate sources. The $\delta^{18}\text{O}$ - NO_3 may be quite different depending on whether the source of oxygen is completely atmospheric, such as with ammonium-nitrate fertilizer, or a combination of groundwater oxygen and atmospheric oxygen, which occurs during nitrification of ammonium (Panno et al., 2001). Synthetic nitrate fertilizers are significantly more positive in $\delta^{18}\text{O}$ (+17 to +25‰) (Figure 2) as compared to nitrate from other common sources ($\delta^{18}\text{O} < 10$ ‰) (Mengis, et al., 2001) (Xue et al., 2009), such as $\delta^{18}\text{O}$ - NO_3 from manure ranges from -5 to 2‰ (Wassenaar et al., 2006).

The process of converting ammonium to nitrate by microbial metabolic activities is called “nitrification”. In the process, $\delta^{18}\text{O}$ - NO_3 tends to be lower (-5 to 15‰). During nitrification, nitrogen atoms originate from ammonium (NH_4^+) and/or NO_2^- molecule, while the oxygen atoms originate from O_2 and/or H_2O (Kendall et al., 2008). A theoretical range of $\delta^{18}\text{O}$ - NO_3 values can be calculated based on the $\delta^{18}\text{O}$ - H_2O from local precipitation (Kendall and Aravena, 2000).

$$\delta^{18}\text{O}-\text{NO}_3 = 2/3 \delta^{18}\text{O}-\text{H}_2\text{O} + 1/3 \delta^{18}\text{O}-\text{O}_2$$

Equation 2. This equation is used to estimate the theoretical range of $\delta^{18}\text{O}$ - NO_3 based on local precipitation and atmospheric O_2 .

Atmospheric O₂ has a reported value of 23.5‰ (Kroopnick and Craig, 1972).

There are a number of assumptions when using Equation 2, laboratory conditions are similar to natural soils, no fractionation occurs during formation, the atmospheric O₂ used in the calculation is equal to the atmospheric average, and that the $\delta^{18}\text{O-H}_2\text{O}$ used is equal to the measured $\delta^{18}\text{O-H}_2\text{O}$ values (Kendall and Aravena, 2000). Often it has been found that the $\delta^{18}\text{O-NO}_3$ is a few per mil higher than expected when using Equation 2 because of changes in the proportion of oxygen from water and O₂ sources, or because of evaporation or seasonal changes in precipitation $\delta^{18}\text{O-H}_2\text{O}$ (Kendall et al., 2008). Nitrate derived from nitrification of ammonium or urea-based fertilizers is typically characterized by $\delta^{18}\text{O}$ values less than 15‰, with most having $\delta^{15}\text{N}$ around 0‰ (Mayer et al., 2002).

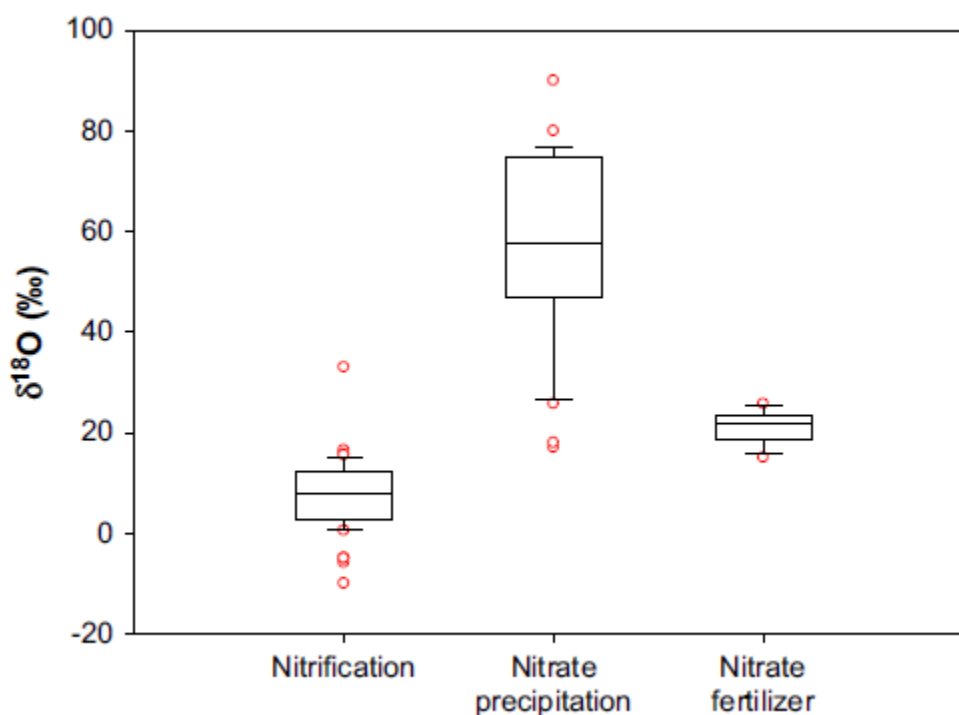


Figure 2. Box plots of $\delta^{18}\text{O-NO}_3$ values from nitrate generated during nitrification, nitrate atmospheric precipitation, and nitrate fertilizer. Box plot illustrates the 25th, 50th, and 75th percentile; whiskers indicate the 10th and 90th percentiles; and circles are data outliers. From Xue et al., (2009)

Since oxygen and nitrogen isotopes fractionate at a relatively constant ratio to one another during denitrification, it is possible to use both isotopes in conjunction with each other to help determine the sources of nitrate and whether denitrification has occurred in the groundwater system (Panno et al., 2001). Using both isotopes together can yield even more accurate nitrate source identification, especially if isotopic values fall in a range which correlates to multiple source. Plotting the two values against each other (Figure 3) can be a very powerful tool in determining possible sources.

Mengis et al. (2001) discuss how fractionation can occur with $\delta^{18}\text{O}\text{-NO}_3$ due to slow moving nitrate through the vadose zone being affected by microbial immobilization and which situations are appropriate for using $\delta^{18}\text{O}\text{-NO}_3$ as a direct tracer. They determined that soils with higher percentages of fine-grained sediments had greater chances of microbial interaction and fractionation of the isotopic composition. For Edgar, this is not too much of an issue because more than half of the vadose zone is comprised of sand or sand/gravel with only thin layers of sandy silt/clay, thus vertical movement is relatively quick. Microbial interaction would only be a concern towards the top of the vadose zone, near and just below the root zone. In these finer grain materials, carbon is more likely to reside due to lower hydraulic conductivities and slight charge imbalances. Carbon plays a significant role in creating anaerobic conditions required for denitrification (consumption of O_2) and acts as an electron donor for nitrate reduction (Kendall et al., 2000).

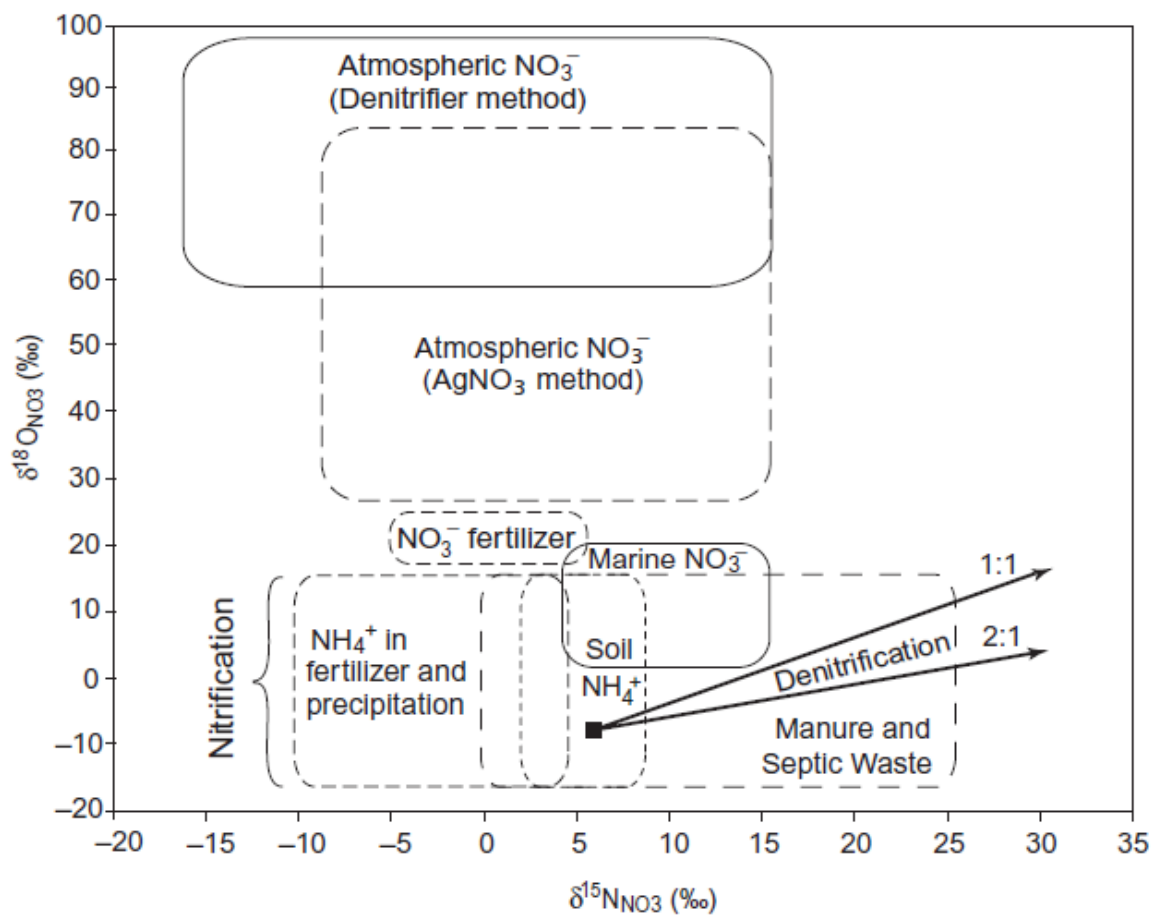


Figure 3. Combined Nitrate Sources Determination Using $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from various source. The typical ranges of $\delta^{18}\text{O}$ values produced by nitrification on ammonium and organic matter are denoted by “nitrification” (Kendall et al., 2008)

Water

The $\delta\text{D-H}_2\text{O}$ (deuterium) and $\delta^{18}\text{O-H}_2\text{O}$ are the most conservative tracers available, because in this case, the isotopes being measured are the water itself, rather than another compound/molecule dissolved in the water (Simpkins, 1995). Water isotopes in groundwater are a general reflection of the isotopic values in the local precipitation. Due to the position within the continent, Nebraska's climatology is in the region of where competing airstreams (Arctic airstream, Tropical airstream, and the Pacific air wedge) meet and are affected by the seasonal changes associated with each of the airstreams. (Harvey and Welker, 2000). Nebraska's precipitation comes primarily from two moisture sources, the Gulf of Mexico, and the Pacific Ocean or a mixture of both, with nearly 80% of the moisture having a Gulf source (Harvey and Welker, 2000).

Generally, water retains its stable isotopic signature unless diluted or mixed with waters of a different isotopic composition. (Yin, et al., 2011) Uses for these environmental tracers include: determination of groundwater mixing; seasonality and sources of recharge; and rate of groundwater evaporation (Hendry, 1988). Due to thermodynamics, it is preferentially easier for lighter isotopes to evaporate compared to heavier isotopes, since less energy is required to change phases, thus a relative enrichment of $\delta^{18}\text{O-H}_2\text{O}$ and δD as compared to normal precipitation/unevaporated groundwater. Evaporation is the most common form of fractionation of water isotopes, but others can occur as the results of condensation, freezing, melting, chemical reactions, or biological processes (Freeze & Cherry, 1979). Measurement of water isotopes can lead to an approximation of the season in which the majority of the water reached the water table based on the isotopic ratios of the average local precipitation. The ratios of

δD and $\delta^{18}O-H_2O$ are preserved upon arriving at the saturated zone and little fractionation occurs afterwards.

A linear relationship between δD and $\delta^{18}O-H_2O$ was discovered by Epstein and Mayeda (1953) and Friedman (1953). Isotope values are plotted and compared to the international standard, Vienna Standard Mean Ocean Water (VSMOW), for which line equation is $y=(8x)+10$. Depending on the how data plots compare to the standard line, a determination can be made as to whether the sample has been victim to evaporation (where the sample is enriched with heavier isotopes relative the major isotope). Local water lines have been determined from Mead, Nebraska ($y=7.4x+7.32$) (Harvey, 2001), and North Platte, Nebraska ($y=7.66x+4.96$) (Harvey and Welker, 2000). These lines are generally close to the VSMOW line, but differ because the Vienna water line is based on a global average. Comparison of these region lines to those from the study area should reveal differences due to altitude, latitude, temperature, and amount of precipitation (Yin et al., 2011).

Temperature is inversely related to the isotopic fractionation that occurs during condensation and evaporation (Mazor, 2003). This means that isotopic ratios of δD and $\delta^{18}O$ will be more enriched during warmer periods of the year, and more depleted during cooler periods.

2.1.3 Hydrogeochemistry and Trace Metals

The major ions present in the groundwater can give insight into the overall chemistry of the system, and are used to show major contributions of different groundwater sources. These are the major constituents in most groundwater systems and

can tell quite a bit about the chemistry of the groundwater and what sort of environment it has traveled through. Major cations are sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg), and major anions include chloride (Cl), sulfate (SO_4), and bicarbonate (HCO_3), along with minor anions including bromide (Br), fluoride (F), and phosphate (PO_4). Geochemical differences from samples collected at the same location at different times of the year can give evidence that water from different sources or possibly depths in the water column are being drawn into the well.

The classification of water is based on the major cations and anions dissolved in the water, this allows for the determination of the minerals they likely originated from. The most common water origins are either from gypsum (CaSO_4) or calcium bicarbonate $\text{Ca}(\text{HCO}_3)_2$, calcite (CaCO_3) can also be a source material, but is not as soluble as either gypsum or calcium bicarbonate. If the water is very deep where brines are known to exist or near an ocean or sea, where there is salt water intrusion into the groundwater system, halite (NaCl) can be a predominant source. Gosselin, et al., (2001) discusses dissolved ions and their various sources in eastern Nebraska and southern South Dakota. In the southern portion of the study area (including Fillmore, Saline, Jefferson, and Gage counties in Nebraska), it was determined that the predominant water present was of Ca- HCO_3 , Ca-Na HCO_3 , and NaCl type waters.

Using a program produced by the USGS called PHREEQC (Parkhurst & Appelo, 2013), solubility and saturation indices can be calculated by inputting ion concentration, pH, and temperature data from samples. The output results show likely source materials based on the input data, and the apparent saturation/undersaturation of each mineral.

Trace Metals

Recent studies by other researchers at the University of Nebraska have shown a link between the presence of nitrate and uranium. Nolan & Weber (2015) present evidence that there is a strong correlation between the presence of nitrate in groundwater and the recent mobilization of naturally occurring uranium in the soil. These researchers discuss how high nitrate allows biotic and abiotic processes to occur that allow uranium to be mobilized in groundwater. In locations such as Hastings, NE (approximately 42 km north-west of Edgar) where pore water vadose zone nitrate levels have been reported to be averages of 10.66 mg-N/L, 14.88 mg-N/L, and 18.73 mg-N/L, for irrigated lawns, pivot-irrigated farmland, and gravity irrigated farmland, respectively (Adams, 2018). Hastings has also seen high levels of uranium in their municipal and domestic wells. Hastings Utilities have funded many research projects that investigate both high nitrate in the vadose and phreatic zones, but also the recent mobilization of uranium.

3.1 Study Area

The village of Edgar has a population of 498 people according to the 2010 U.S. census. The village has two municipal wells that are approximately half a mile apart that are used to supply drinking water to the residents and businesses. At any one time, only one of the two municipal wells is active. After using one of the wells for twelve weeks or so, the city switches to other well to allow the groundwater to recover.

3.1.1 Sample Locations

The majority of the wells are located inside the city of Edgar, with the exception of a few wells outside the city limits, both up and down gradient of the municipal wells (Figure 4). Since the groundwater gradient is northwest to southeast, the wells tend to follow the same direction as the gradient in order to better evaluate upgradient to downgradient variability. The majority of the samples were collected from dedicated monitoring wells, with the exception of a few that were collected from selected domestic wells. The site with the best vertical resolution has a set of three dedicated monitoring wells located adjacent to the southernmost municipal well and spaced at five foot intervals. Many of the wells were adjacent to, or in the middle of an agricultural field, but there are a several wells located inside the city limits. Collecting samples from both types of land use can help narrow down the source(s) of contamination and their possible locations.



Figure 4. Sample locations and WHPA of Edgar, Nebraska.

3.1.2 Geology and Hydrogeology

Geology

The geologic formation of the aquifer used by Edgar ~~is fairly straightforward,~~ consisting of early Cretaceous to Tertiary-age bedrock that is overlain by unconsolidated Pliocene to Quaternary-age sediments (Little Blue NRD, 1996). The unconsolidated material overlying the bedrock ranges from silts and loess to sand and gravel, indicating a fluvial depositional environment. Although the greatest thickness consists of sand and

gravel, in most places this layer is sandwiched between layers of mostly silt and loess.

Figure 5 shows a detailed cross sections constructed from test hole data collected by the University of Nebraska –Lincoln (UNL) Conservation and Survey Division and assembled by the Little Blue NRD. Edgar is located near the crossing of B-B' and E-E'. The sand and sand/gravel portion is where the most prolific portion of the aquifer is located; it supplies water for municipal, domestic, and irrigation use.

Figure 6 was constructed from the well logs of several of the wells sampled for this project. The cross section runs nearly parallel with groundwater flow, from northwest to the southeast. The upper most section, near the surface, is composed of silt and loess for roughly 35 feet followed by around 150 feet of sand and gravel with the occasional interbedded discontinuous silt/clay lenses. The groundwater gradient across the section has less than a five foot difference, making it difficult to display across the length of the approximately 1.33 mile section. Although samples were collected beyond both ends of the cross section, no soil core data is present from these sites because they are domestic wells. Before September, 1993, when domestic wells were drilled, it was not required that they be registered with the Nebraska Department of Natural Resources, so for many of the domestic wells located in the Edgar area, there is no known record of the sediments textures.

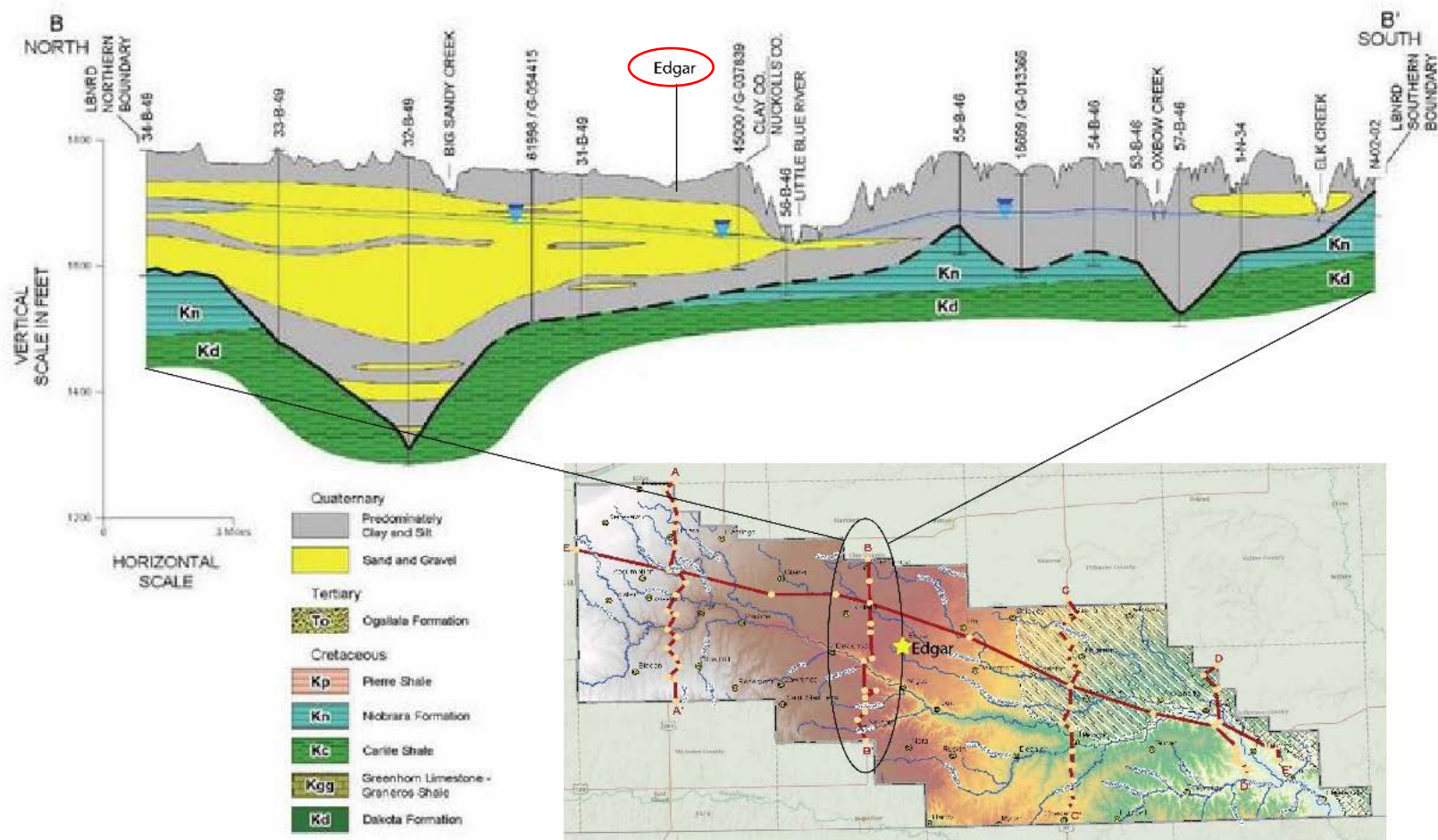


Figure 5. Little Blue NRD with Selected Cross Section (Little Blue NRD, 1996)

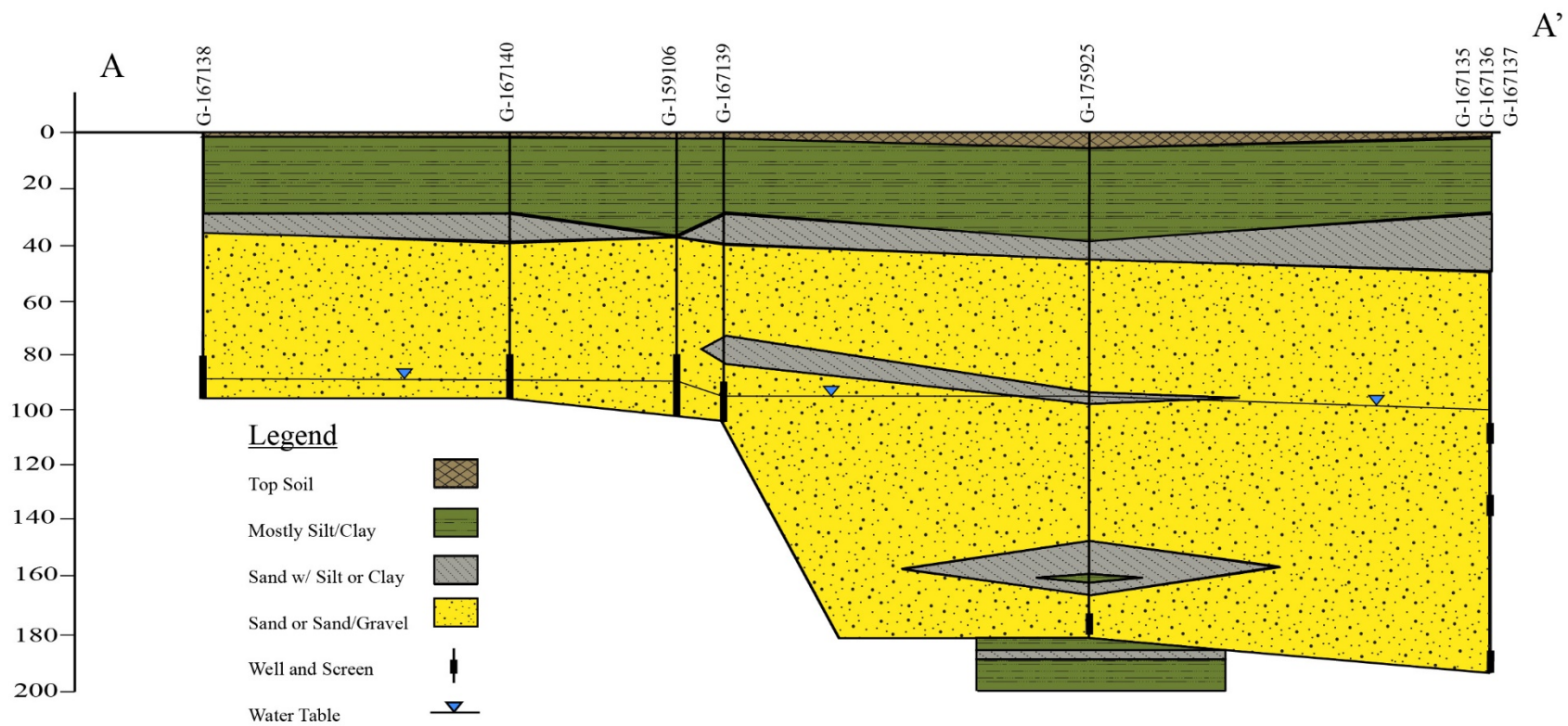


Figure 6. Edgar Cross Section A-A'

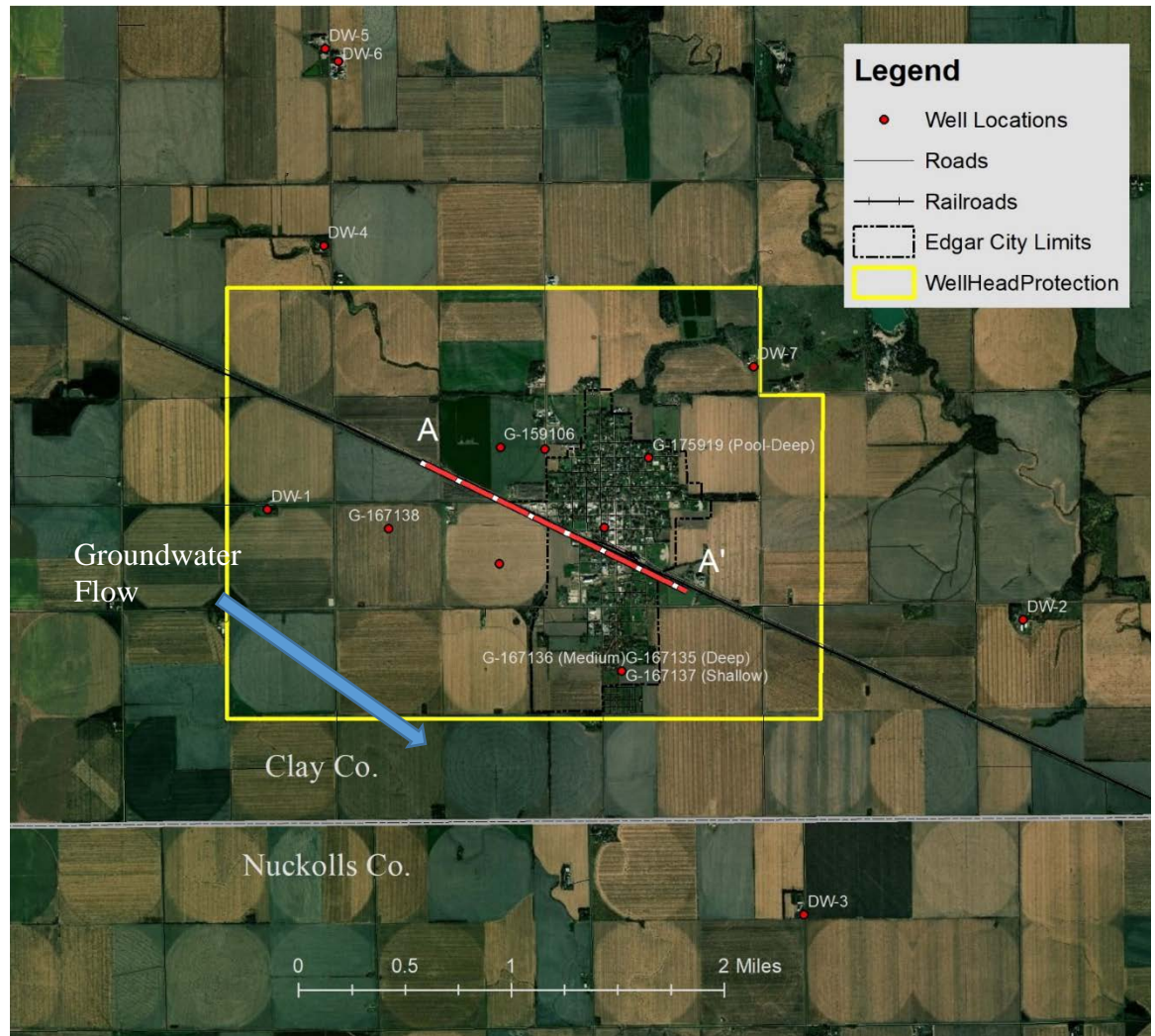


Figure 7. Map View of Cross Section Line A-A'

Hydrogeology

The hydrogeologic conditions were a major focus in the pilot study conducted by Olsson Associates, 2011. The overall thickness of the unconsolidated zone, in the study area ranges from approximately 100 to 175 feet thick of mostly Quaternary-age sand and gravel with interbedded layers of silt/clay. These sediments are considered to be part of the High Plains aquifer (Gutentag et al., 1984) and were deposited by a former channel of

the Platte River that was aligned from west to east several miles south of the modern-day Platte River Channel.

In their report, Olsson Associates (2011) determined the local flow gradient was toward the southeast, with the hydraulic conductivity ranging from around 400-600 ft./day, in the sandier portions of the saturated material. These values agree with accepted values for hydraulic conductivity for sands and gravels and supports the description of the subsurface in the cross sections completed and published by the (Little Blue NRD, 1996). The aquifer material has an estimated storage capacity 0.11 by aquifer pump test (Olsson Associates, 2011). The range of storage capacity is 0.1-0.3 in unconfined aquifers, such as the one lying under Edgar, and is roughly equal to that of the specific yield, because virtually all the water is released due to gravity, rather than by any overlying burden caused by extra pressure from a confining layer (Lohman, 1972). The depth to water was determined during sampling to be approximately 90 feet (+/- 5 feet) below the surface; the water level has fallen by roughly 15 ft since reported in Keech & Dreeszen (1959), probably due to continuous years of extensive irrigation.

Since most sediment in the vadose zone is comprised of sand or gravel, once the water and nitrate pass the root zone (approximately 7-8 ft) and the relatively thin layer of mostly silt/clay, the transport rate of the nitrate is estimated to be equal to that of water ($K_d=1$).

3.1.3 Vadose Zone

The vadose zone is roughly 90 to 100 feet thick throughout the Edgar area. Spalding and Jensen (2010) conducted a vadose study of Edgar where they investigated

nitrate loading, soil concentrations, and pore-water concentrations. They identify likely point sources of nitrate inside the WHPA and likely within the capture zone of the city municipal wells. Active and inactive barnyards as well as a grain waste dump site had the highest soil nitrate concentrations, routinely reaching 100 $\mu\text{g/g}$ and occasionally 150 $\mu\text{g/g}$, and the pore water beneath the sites approached 1000 mg/L (Spalding and Jensen, 2010). Nonpoint sources of nitrate in the vadose zone can also be higher than the MCL, but are generally lower in concentration compared to the point sources. The non-point source locations in Edgar are the widespread center pivot irrigated fields which are fertilized yearly (unless allowed to be fallow). Spalding and Jensen (2010) also discuss how it is common for large pulses of nitrate to be present deep in the vadose zone resulting from early rains that leach nitrogen fertilizer too quickly for crops to uptake the nutrients, but this might not be the case since most of the fields are irrigated so the rate at which the water moves through the root zone is more controlled. In addition, the top 45 feet of the vadose zone is comprised of silt/clay material, which does not lend itself to very high hydraulic conductivity.

The report by Olsson Associates (2011) details the findings of site 28 (near the southern municipal well where the nested well that was sampled for this project is located) in the report by Spalding and Jensen (2010). A pulse of nitrate ($>50 \mu\text{g/g}$) was found at a depth of 14 feet in the 2010 sampling that was not present in the 2005 sampling, though perhaps the beginning of the pulse can be seen near the surface of the 2005 coring. They concluded that the pulse would take close to 37 years to reach the water table, assuming the same constant downward movement determined from the two sampling periods. This estimate is an over estimate of transit time to reach the water

table. The rate of movement (~ 2.4 ft/yr) calculated from the two sampling times only reflects the rate in silt/clay portion of the vadose zone, which only extends for approximately 40 feet. Past this point, the remainder of the vadose zone (approximately 45 feet) consists of sand and gravel, which would drastically increase the vertical transport rate. The pulse would reach the sand and gravel portion in approximately 19 years, and only an additional few weeks to move through the material with the higher hydraulic conductivity.

Site ID	Land Use Description*	2010 Total Nitrate-N (lbs/acre)	2005 Total Nitrate-N (lbs/acre)
E-2	Irrigated corn/soybean	750 (6-36')	474 (6-36')
E-3	Abandoned barnyard	8,116 (6-45')	8,426 (6-45')
E-4	Gravity irrigated corn	803 (6-38')	304 (6-38')
E-6	Sewage plant lift station area	535 (6-38')	70 (6-38)
E-8	Irrigated corn/soybean	712 (6-45')	689 (6-45)
E-10	Abandoned barnyard	6,503 (6-30')	10,440 (6-30')
E-12	Native grass on border of corn field	588 (6-30')	93 (6-30')
E-13	Old junk yard	242 (6-24')	76 (6-24')
E-14	Dryland wheat/corn/soybeans	541 (6-40')	488 (6-40')
E-18	Corner of fertilizer plant	633 (6-26')	3,316 (6-26')
E-19	Residential lawn.	674 (6-45')	97 (6-45')
E-21	Corn/soybean gravity irrigated	461 (6-25')	152 (6-25')
E-22	Side of abandoned RR surface water drainage area	372 (6-45')	134 (6-35)
E-25	Corn/soybean rotation gravity irrigated	1,094 (6-50')	861 (6-50')
E-28	Pivot irrigated corn near Municipal well	1,908 (6-50)	324 (6-50')
E-32	Grain Elevator waste dump	11,037 (6-40)	347 (6-40')
E-33	Grass and tree waste dump	260 (6-25)	67 (6-23')
E-40	Active Barnyard	3,098 (6-25')	2,975 (6-25')

Table 1. Edgar Land Use and Vadose Zone Nitrate Loading over select intervals. (Spalding and Jensen., 2010)

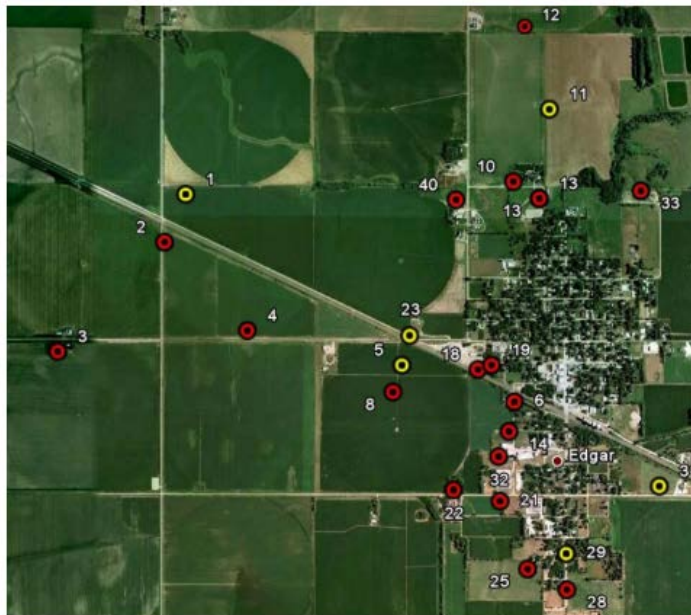


Figure 8. Edgar Land use. 2005 coring sites (red and yellow) and 2010 coring sites (red only) (Spalding and Jensen, 2010)

3.1.4 Land Use

The entirety of the land use, upgradient from Edgar groundwater recharge zone, is used for agriculture, with the exception of isolated homes. Crops in the Edgar area are typically planted in corn or soybeans (both dryland and irrigated), with a few fields of wheat (Spalding et al., 2010). In addition to the residential lawns, there are also active and abandoned barnyards, old junk yards, wastes sites for trees, and a grain elevator dump site (Table 1). Figure 8 shows the spatial distribution of the different land use types. Points of concern are the two abandoned barnyards (E-3 and E-10) and the active barnyard (E-40), as these locations were reported to have the highest total nitrate in each respective interval in the vadose zone in both vadose coring years. These three sites are likely point sources for nitrate contamination, whereas the other sites are non-point sources due to their large areal extent and lower level of applied nitrate.

4.1 Methods and Procedure

4.1.1 Sample Collection

Upon removing the well cap, each monitoring well was allowed to “breathe” for several minutes to ensure the water level was at equilibrium before any pumping commenced. Next, a water level indicator was lowered in the well to record the water level at equilibrium. Once recorded, a submersible pump was lowered to the approximate middle location of the documented screen portion. In wells that were screened at the very bottom of the casing, pumping from a few feet above the bottom kept any sediment/mud from being pumped. A Hydrolab MS5 multiparameter water quality sonde was installed in line with the pump (probe kept on the surface), so that temperature, pH, conductivity, and dissolved oxygen could be recorded at the time of sampling. In order to obtain a “fresh” sample, the submersible pump was allowed to pump for 10-15 minutes to ensure the water that was at stable conditions (temperature, pH,...etc.) and that fresh formation water was being collected, rather than water (with possibly altered chemistry and isotopic ratios) that was sitting in the well casing. Samples for nitrate concentration, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}\text{-NO}_3$, δD and $\delta^{18}\text{O}\text{-H}_2\text{O}$, and major ions were collected in 1-liter acid-washed polyethylene bottles, which would be later subsampled in the lab for each respective protocol.

The seven sites where samples were collected from domestic wells followed shorter sampling procedures. Since sampling occurred from a location that already had a pump in place, sample collection took place when temperature and pH were steady.

In order to get a more complete picture of the nitrate concentrations and isotope ratios, samples were collected with irrigation season in mind. There are numerous irrigation wells present all around and in Edgar. During the growing season (summer and early fall) irrigation wells have a notable impact on the groundwater system, drawing water into the well from different depths than where the screen is located. As a result, sampling only during a single season can give a skewed view of the groundwater system. Samples were collected during three different times of the year, December, May, and August. These times were chosen in an attempt to catch the groundwater system at different stages of irrigation. December was chosen because irrigation had concluded three months prior and the water table had been allowed to recover. May was chosen because irrigation had just begun and the water table had just recently started to move. August was chosen because irrigation wells had been pumping for several months and the end of the growing season was near. At this point the water table has fluctuated the most and could possibly be pulling water into the wells from higher in the water column, causing a mixture of water from different groundwater recharge events and seasons.

4.1.2 Nitrate

The concentration of nitrate was determined using a Seal AQ2 discrete auto-analyzer. Using a combined method, nitrite and nitrate are analyzed together as if they were all nitrite. The nitrate (NO_3) is reduced to nitrite (NO_2) by passing the sample through a cadmium coil, which results in one of the oxygens being stripped away. After reduction the NO_2 is reacted with sulfanilamide in the presence of N-(1-naphthylethylenediamine) dihydrochloride (EPA 127). The sample is then analyzed colorimetrically using a spectrophotometer. The nitrate reacts with and forms a pink

solution, the higher the concentration, the darker the solution will become. The maximum calibration range of the AQ2 is 2 mg/L, though many groundwater samples are higher than this limit. The instrument runs each sample at full strength (undiluted) and if necessary will dilute the sample 10x or even 100x in rare occasions.

The analysis to determine the likely source(s) of nitrate in the groundwater depends on both the $\delta^{15}\text{N}$ and $\delta^{18}\text{O-NO}_3$. The $\delta^{15}\text{N}$ was analyzed following the method developed by Gormly and Spalding (1979). In this method, the concentration of nitrate is measured by reducing nitrate to ammonia using Devarda's alloy, by steam distillation, and titration. The acidified ammonium in the distillate is concentrated and reacted with lithium hypobromite to form nitrogen gas and purified from all other contaminants on a glass vacuum preparation line. Once a pure gas is obtained, it is sealed in a glass vial and analyzed on an Optima dual inlet mass spectrometer, where the isotope composition of nitrogen gas is precisely determined. The sample gas is compared to a working standard gas of known isotopic composition that has been calibrated against an international standard.

The determination of the $\delta^{18}\text{O-NO}_3$ follows the method described in Chang et al. (1999). The water sample is first passed through an ion exchange column, then the nitrate is eluted from ion exchange resin with 3 molar hydrochloric acid (HCl), neutralized with Ag_2O , and dried to get a solid silver nitrate precipitant. The silver nitrate can then be analyzed for oxygen isotope ratios (i.e. $\delta^{18}\text{O-NO}_3$) on the Elemental Analysis mass spectrometer. The isotopic ratios are calibrated using USGS34 and USGS35 reference materials, with values of -28‰ and +57‰ respectively.

4.1.3 Water

For $\delta^{18}\text{O}$ -H₂O analysis of water, the samples were analyzed following the method described in Epstein and Mayeda (1953). The water is injected with CO₂ and equilibrated for 15 hours at 40°C. Once equilibrated, the gas is let into the dual Inlet mass spectrometer where the CO₂ concentrations are determined by their masses (44, 45, and 46) and are compared to other reference and standard gases. The ²H in water is analyzed by reducing the water to hydrogen gas by passing the water over chromium metal at temperature exceeding 1000°C (Morrison et al., 2001) and carried by a helium stream to the detector and calibrated against international standards.

4.1.4 Major Ions and Trace Metals

Cations

The major cations analyzed are calcium, magnesium, potassium, and sodium. These concentrations were determined using atomic absorption spectrophotometry on a Perkin Elmer AAnalyst 400. The sample was drawn in and nebulized into an acetylene/air flame, with an optical beam emitted at a wavelength of light that is specific to an individual element. When the ionized sample passes through the flame, the amount of the optical beam that is absorbed is proportional to the elemental concentration in the sample (Hill & Fisher, 2017). Each sample was filtered and diluted 10x to ensure the absorbance was within the calibration range.

Anions

The major anions analyzed are chloride, fluoride, bromide, phosphate, sulfate, nitrite, and nitrate. The analysis was performed using a Dionex ion chromatograph with

an autosampler, following the method described in (Pfaff, 1993). Each sample was first filtered to remove any suspended solids or other debris that might clog the needle or tubing. The sample is passed through an anion column, where the anions are separated on an AS14 ion exchange column. Their peak intensity is integrated to find an area, which is associated to the standard calibration. Because multiple anions were analyzed with different natural concentrations, each sample was analyzed at full strength (undiluted) and with 41x dilution.

Trace Metals

Samples were analyzed for uranium and selenium using a GVI Platform XS inductively coupled plasma mass spectrometer (ICP-MS). The reporting limit for uranium is 0.1 µg/L and 0.5 µg/L for selenium. Since the metals were already dissolved in the water, no digestion was required in order to get them into solution. The samples were filtered to ensure that no particulates were allowed into the instrument. Once the auto sampler had drawn the sample into the instrument, the water is then passed through a plasma torch that is roughly 10,000 K, which vaporizes and ionizes the water and dissolved solids. The ionized solids are then detected on the mass spectrometer and then compared to a calibration against known concentrations.

5.1 Results and Discussion

The first field data collected was static water level. Water level was measured during each sampling period (Table 2). Water levels in December and August were very close in many of the samples, with a difference of less and half a foot. The highest water level for each well was in May. This could be the result of allowing the water table to fully recover from the previous year's irrigation. When the May samples were collected, irrigation was just beginning and not likely to have affected the groundwater level to a noticeable degree, or the water level had peaked at a higher level earlier and was already declining. Based on monitoring the vadose nitrate movement in the vadose study by Spalding and Jensen (2010), it is unlikely that the rise in the water table was caused by early spring rains of the same year. An effort was made to investigate the seasonality of the water table fluctuations, but the local USGS wells, though generally sampled yearly, only had one data point a year, usually in April.

Basic water properties such as temperature, pH, and specific conductance (SpC) collected from the Hydrolab can be found in (Table 2). Out of courtesy to the property owners of the domestic wells, the designation "DW" (Domestic Well) is used in lieu of their real names. Changes in simple water properties can provide clues to different process that might be occurring in the subsurface. Temperature, though lower in December and higher in August, changed little despite the changes in season. Over all the lowest recorded temperature was 12.59°C and the maximum 16.80°C. These differences simply reflect the air temperature on the land surface where the water was collected. Warmer air temperatures in August and colder temperatures in December could account for the differences. Though there is a difference of 4.21°C, most of the

samples were closer to the mean temperature of 14.01°C. With such a small temperature range, solubility of dissolved solids and pH are not affected to a degree that would affect any of the results.

Table 2 shows the pH results from each sample. Differences in pH have bigger issues with solubility of both nitrate and major ions. The typical range of pH for ground water is 6.0-8.5. The lowest measured pH 6.39 is within the typical range for groundwater, but the highest value of 9.83 is much higher than is expected. The EPA National Secondary Drinking Water Regulations recommended pH range between 6.5 and 8.5, but this is not enforceable. It is required, however, that users be notified if their water falls outside this range. A value of 9.83 and 9.60 found in wells G-175919 and G-175925 in May 2015 is much too basic in a normal groundwater and does not seem to fit with any of the other samples. This could be the result of not fully developing the well upon installation. At both wells, the casing was sealed using bentonite clay. Like most clays, bentonite is basic with a pH range exceeding 9.0. When sampling commenced, the produced water was cloudier than most other wells, and took more time for the water to become clear. If the well was not developed properly upon installation, then residual bentonite could have still been inside the well casing. When the same two wells were sampled in August, the pH values (7.62 and 7.98) were still slightly higher than average value (7.42), but were much closer and inside the expected range for groundwater.

Well ID	Well Depth (ft)	Screen Interval (ft)	Depth to Water (ft)			pH			Temperature (°C)			SpC (µs)		
			Dec '14	May '15	August '15	Dec '14	May '15	August '15	Dec '14	May '15	August '15	Dec '14	May '15	August '15
G-159106	103	82-103	-	87.7	88.7	-	6.4	6.7	-	14.0	13.8	-	879.2	673.2
G-167135	185	175-185	98.1	97.5	98.2	6.9	7.2	6.9	13.0	14.2	14.0	749.9	737.9	746.7
G-167136	140	130-140	98.1	97.6	98.3	6.8	7.2	7.0	12.7	14.3	13.9	754.5	769.7	778.4
G-167137	110	100-110	97.8	97.2	97.7	7.0	7.1	7.3	12.8	16.8	14.7	849.7	855.2	842.7
G-167138	98	83-98	89.1	88.2	89.2	7.1	6.9	7.2	12.6	14.9	13.5	851.2	879.2	933.7
G-167139	107	92-107	98.5	97.6	98.9	7.3	6.8	7.0	12.8	14.2	15.2	827.7	827.4	778.7
G-167140	98	83-98	90.2	89.4	90.1	7.2	6.7	7.1	13.0	14.4	13.8	764.5	797.1	774.4
G-175919	177	172-177	-	91.0	91.7	-	9.8	7.6	-	14.8	14.1	-	481.5	461.2
G-175925	177	172-177	-	95.6	96.3	-	9.6	8.0	-	14.8	15.6	-	508.7	518.0
DW-1	-	-	-	-	-	-	6.7	7.8	-	13.2	14.1	-	787.4	914.3
DW-2	-	-	-	-	-	-	-	7.4	-	-	13.7	-	-	684.8
DW-3	-	-	-	-	-	-	-	7.5	-	-	13.4	-	-	845.9
Municipal	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DW-4	-	-	-	-	-	-	-	8.1	-	-	13.7	-	-	496.2
DW-5	-	-	-	-	-	-	-	8.2	-	-	14.2	-	-	889.9
DW-6	-	-	-	-	-	-	-	8.4	-	-	14.7	-	-	625.6
DW-7	-	-	-	-	-	-	-	8.5	-	-	13.1	-	-	789.6

Table 2. Well descriptions and basic sample water properties

5.1.1 Nitrate

Of the 33 samples collected, 25 exceeded the MCL of 10 mg-N/L (Table 3). The highest concentration occurred in the August sample from DW-1 on the west side of town with a concentration of 26.0 mg-N/L. The lowest reported value of 4.28 mg-N/L was from a sample collected in May from well G-175919. The average nitrate value of the 33 samples is 14.19 mg-N/L. When each location is compared over time a trend appears: higher concentrations in August and lower concentrations in December (Figure 9). Variations in nitrate concentration over time might indicate that nitrate concentrations are not homogenous throughout the water column. Differences such as seen with DW-1, show a dramatic increase of 78% indicates that the water column is not completely uniform throughout with respect to nitrate concentration. Based on previous nitrate measurements in recent years, concentrations have been slowly increase for many of the wells in and around Edgar.

There are two wells that have very similar nitrate concentrations from different times of the year. Wells G-175919 and G-175925 both report values that are below the MCL in both May and August. The May concentrations are 4.28 mg-N/L and 4.93 mg-N/L respectively, and the August concentrations are 5.26 mg-N/L and 6.16 mg-N/L. The location of these two wells are inside the city limits, one located at the old City Hall building and the other near the municipal swimming pool as shown in Figure 12 and Figure 13. It would seem that being inside the city limits might have an effect on any fluctuations in concentrations since there is less nitrate being loaded above the wells, and any influence from irrigation wells is kept to a minimum. However well G-159106 also has almost no change from May to August, 9.59 mg-N/L and 9.64 mg-N/L respectively,

even though it is in the middle of agricultural field with a center pivot so nitrate fertilizers can be assumed to be added to the field to ensure crop growth.

Well ID	Nitrate (mg/L)		
	Dec '14	May '15	August '15
G-159106	-	9.6	9.6
G-167135	14.5	10.7	14.9
G-167136	15.2	13.0	17.5
G-167137	14.8	16.9	17.4
G-167138	19.4	19.7	24.2
G-167139	18.3	18.8	15.5
G-167140	12.4	12.0	12.6
G-175919	-	4.3	5.3
G-175925	-	4.9	6.2
DW-1	-	14.6	26.0
DW-2	-	-	7.1
DW-3	-	-	22.0
Municipal	-	-	11.1
DW-4	-	-	5.9
DW-5	-	-	25.2
DW-6	-	-	10.0
DW-7	-	-	18.6

Table 3. Edgar Groundwater Nitrate Concentrations

Two of the wells with the highest nitrate concentrations are located near each other. Well G-167138 and DW-1 are located on the western side of the WHPA and are among the highest concentrations during each sampling period indicating that the nitrate concentrations are consistently higher in this portion of the WHPA. Well G-167139 is to the southeast of G-167138 (in the direction of groundwater gradient) and though it has higher concentrations than many of the other wells, its concentrations are not quite to the

level of other two. This might be because the nitrate in the groundwater has not yet reached well G-167139.

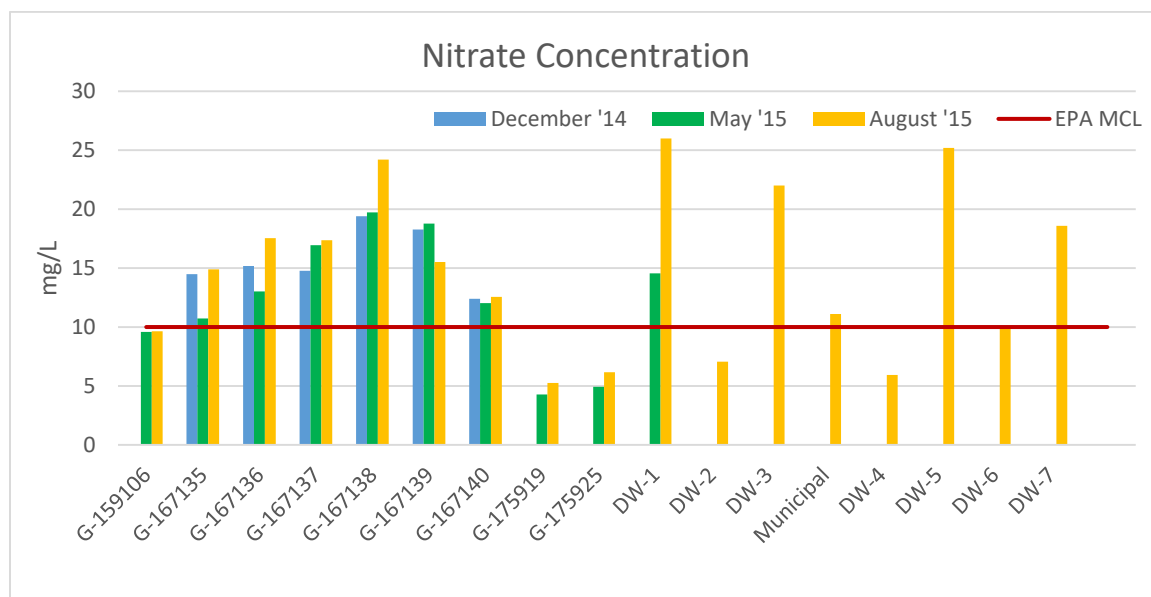


Figure 9. Groundwater Nitrate Concentration Comparison.

Further down gradient, the nested wells G-167135, G-167136, and G-167137 are located next to the southern municipal well. Since the wells are paced roughly five feet apart and screened at different intervals throughout the water column, they provide a great look at the water quality at the different depths. Table 1 shows the depth and screen interval for each of the three wells. G-167135 (deepest) is consistently lower in nitrate concentration as compared to the two adjacent shallower wells. This is not uncommon as deeper water tends to be older and less vulnerable to contamination due to longer flow paths, but does see a slight increase in concentration, likely a result of minor mixing of different waters possibly when sampling occurred drawing water into the well from different depths. Figure 10 demonstrates how deeper wells in an unconfined aquifer tend to have older water because the flowlines leading the screened interval has water that has

been in transit for much longer period of time compared to shallower flowlines. Wells G-175915 and G-175925 are both relatively deep wells too, with screen intervals at 177 feet below the surface, and their distance from any major drawdown from an irrigation or municipal well could both be reasons as to why their nitrate concentrations are kept low.

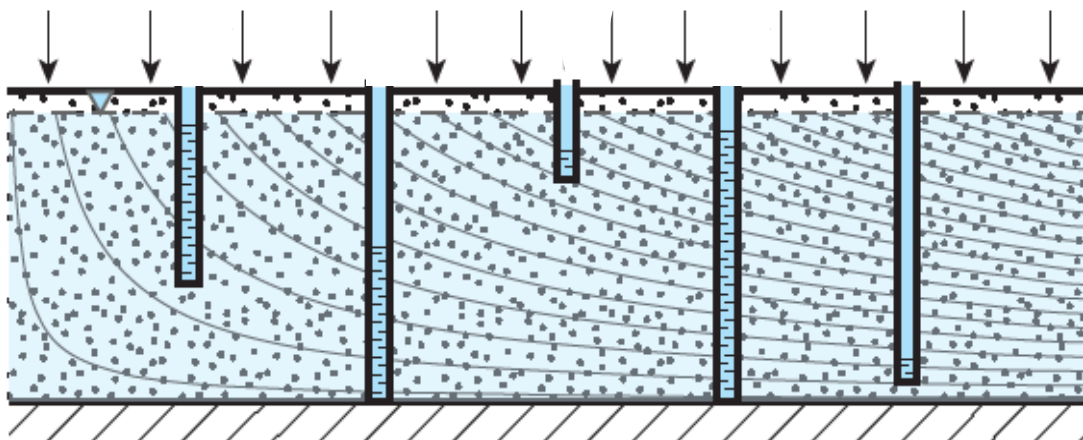


Figure 10. Conceptual Model of groundwater flow paths in an unconfined aquifer.
Source: (Jurgens et al., 2012)

Conversely, the shallower wells tend to have higher nitrate concentrations because they are closer to the surface and more vulnerable to nitrate loading from directly above and fluctuations in water table depth. Well G-167138 is screened from 83-98 feet below the surface, but the depth to water is 88 feet, thus a portion of the screened interval is above the saturated zone. Wells like this may provide clues to the processes occurring at and near the water table. This well also saw one of the highest of any reported concentrations (24.20 mg-N/L) in August. This shallow well shows there are season effects of nitrate at the water table, likely a result of leaching of nitrate from earlier in the season. Other studies such as Zhang, et al., (2014) also reported seasonal changes in

nitrate concentrations where intense application of nitrogen fertilizers coupled with irrigation might be responsible for the enrichment of surface and groundwater. Unlike Edgar where the finer grained sediments at the surface slow the infiltration of nitrate, the study site in Zhang, et al., (2014) reflected the increase of nitrate from the fertilizer applied a month or two previous.



Figure 11. December nitrate concentrations



Figure 12. May nitrate concentration



Figure 13. August nitrate concentration

5.1.2 Isotopes

Nitrate

Nitrate isotopic data are summarized in Table 4. The $\delta^{15}\text{N-NO}_3$ for samples collected in December and May fall in the range typical of synthetic nitrate fertilizer, whereas many of the samples collected in August are outside the characteristic values. Nitrogen isotope values of typical of nitrogen fertilizers generally range from -5 to +8‰, though there are many other sources of nitrate that also partially fall into this range such as ammonia fertilizer, ammonium and nitrate precipitation, and urea. There is an apparent change in the isotope values from many of the wells depending on the time of year sampled. The $\delta^{15}\text{N-NO}_3$ values shift from typical nitrogen fertilizer to what can be described as a mixture of sources. The average value of $\delta^{15}\text{N-NO}_3$ in samples collected in December and May is 4.46 ‰, whereas the August samples is 9.30‰. This is a rather large change in isotopic value. Not all samples collected in August had a dramatic shift, but most did. Well G-167138 reported values of 4.18 ‰ and 2.01 ‰ in December and May, respectively, and a very similar value of 3.79 ‰ in August. In contrast, many wells saw substantial changes, where the isotopic ratio changed by more than 300%. Figure 14. shows a comparison of $\delta^{15}\text{N-NO}_3$ ratios from each well. A trend can be easily shown indicating that many of the wells have elevated $\delta^{15}\text{N-NO}_3$ ratios in August, compared to the other months. Such a drastic change from several reregistered wells indicates that there are different sources of nitrate being drawn down to each well later in the season. Many of the domestic wells were only sampled once, but based on their $\delta^{15}\text{N-NO}_3$ values in August, an argument could be made that those locations also follow the same theory of

multiple nitrate sources or microbial interaction occurring later in the year based on their enriched $\delta^{15}\text{N}$ compared to the values from wells during the previous months.

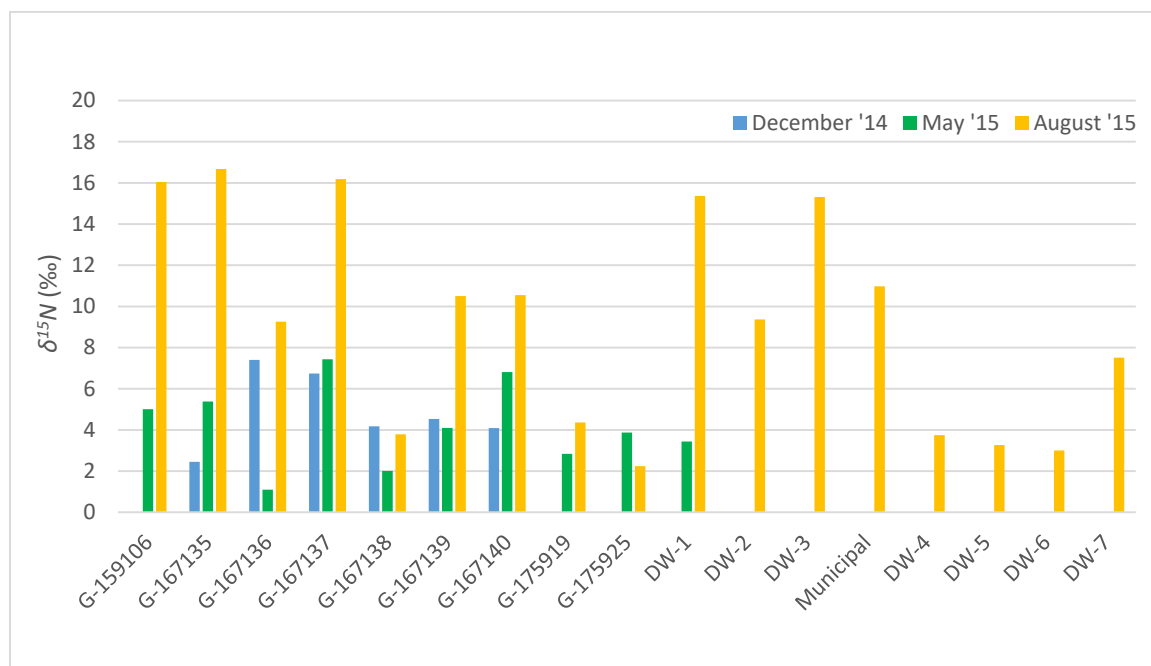


Figure 14. Edgar $\delta^{15}\text{N}$ isotope values

Samples collected at nine wells reported values ranging from +10 ‰ to +17 ‰, which falls into the denitrification or animal waste ranges of $\delta^{15}\text{N}$. The process of denitrification typically corresponds to a decrease in nitrate because the nitrate is being consumed/metabolized and converted to other forms. Since nitrate concentrations are also higher in August, if denitrification is occurring, it not solely the cause of the isotopic shift.

Well ID	$\delta^{18}\text{O-NO}_3$			$\delta^{15}\text{N-NO}_3$		
	Dec '14	May '15	August '15	Dec '14	May '15	August '15
G-159106	-	19.61	16.08	-	5.01	16.04
G-167135	20.66	19.26	16.63	2.45	5.38	16.67
G-167136	19.85	23.55	15.67	7.4	1.1	9.26
G-167137	20.81	20.84	16.67	6.74	7.43	16.18
G-167138	19.29	19.3	18.00	4.18	2.01	3.79
G-167139	18.63	21.12	19.73	4.53	4.1	10.50
G-167140	20.56	19.54	17.84	4.09	6.81	10.55
G-175919	-	19.71	14.41	-	2.84	4.36
G-175925	-	19.57	14.79	-	3.87	2.24
DW-1	-	21.05	15.51	-	3.44	15.37
DW-2	-	-	15.29	-	-	9.37
DW-3	-	-	15.42	-	-	15.31
Municipal	-	-	14.94	-	-	10.98
DW-4	-	-	13.66	-	-	3.75
DW-5	-	-	13.32	-	-	3.27
DW-6	-	-	11.67	-	-	3.00
DW-7	-	-	13.03	-	-	7.51

Table 4. Edgar Nitrate Isotope Values

The land at DW-1 is known to have had livestock in some capacity in the past. Since this location is upgradient from G-167138, G-167135, G-167137, and G-167139, all of which have enriched $\delta^{15}\text{N-NO}_3$ values in August consistent with manure nitrogen. An argument can be made that the elevated concentrations seen in August are from a nitrate plume that originated from an abandoned barnyard at DW-1 in the shallower portion of the aquifer and is mixed with deeper less enriched $\delta^{15}\text{N}$ values. The same is true for wells G-167140 and G-159106. Both of these wells are located near an abandoned barnyard on the north side of town and show enriched $\delta^{15}\text{N}$ in August that is typical of manure. Both of these two sets of wells are located near abandoned barnyards as well as center pivots that create a drawdown effect during irrigation season that pulls

waters down toward the screened portion. As a result, there is likely a mixture of nitrate contaminated water that is from likely different sources the barnyards and irrigation. Again, these sites were reported (Spalding and Jensen, 2010) to have nitrate pore water concentrations nearing 1000 mg-N/L so it is likely that the plume from this point source had just reached the water table and mixes during peak irrigation periods.

Wells G-175919 and G-175925 report low and consistent $\delta^{15}\text{N}$ values in both May and August, despite being down gradient from the northern abandoned barnyard. Both of these wells are located inside town, where there are no irrigation wells nearby (at least 0.5 miles away). The lack of drawdown created by the irrigation wells, along with both of these wells being 177 feet deep would likely result in fairly stable conditions that did not disrupt flow paths or any mix different waters.

The oxygen isotope values show the opposite trend, with samples collected in December and May having slightly higher ratios than those collected during August (Table 4). This also supports the ideas of having a mixture of waters or denitrification. The average value for $\delta^{18}\text{O}-\text{NO}_3$ for December and May is 20.21‰ whereas the average value in August is 15.45 ‰. Unlike the $\delta^{15}\text{N}$ values, $\delta^{18}\text{O}-\text{NO}_3$ values in August are lower in every sample as compared to samples collected in May. Values from each month fall into the range expected for inorganic nitrate fertilizers (15‰ - 25‰). There are two wells, G-167136 and G-167139 that report higher $\delta^{18}\text{O}$ values in May as compared to December, but then follow the same trend of dropping in August (Figure 15).

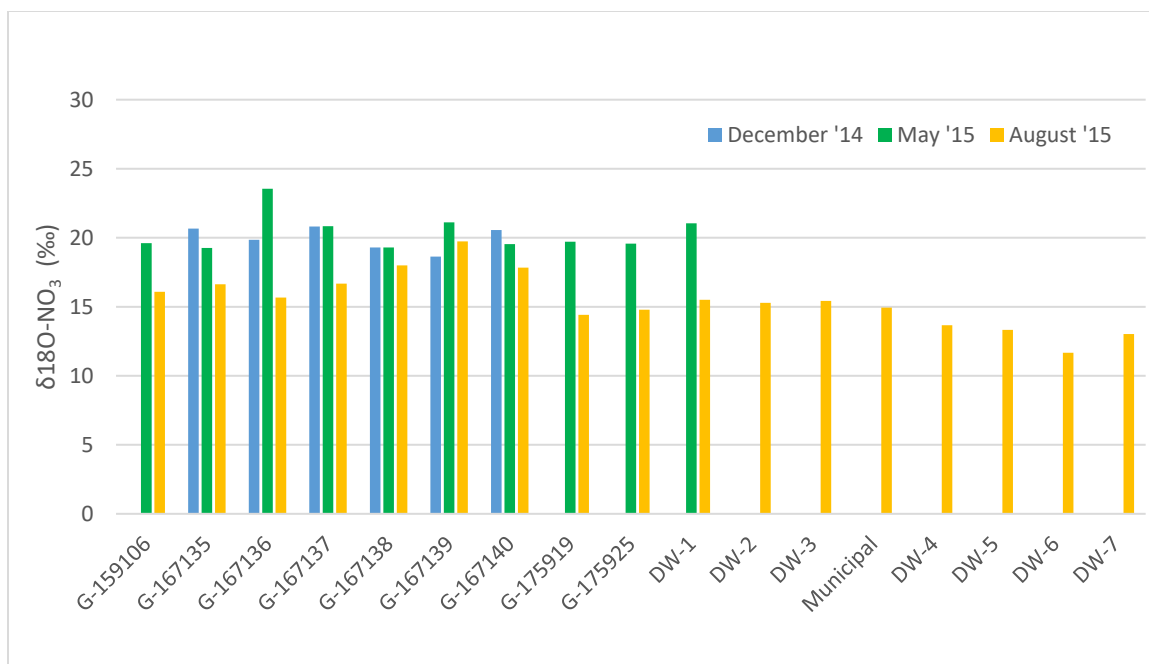


Figure 15. Edgar $\delta^{18}\text{O}-\text{NO}_3$

Nitrification is the process of oxidizing ammonium to form nitrate. During this process, it is assumed that two oxygen atoms from water and one from air (O_2) (Hollocher, 1984). Atmospheric $\delta^{18}\text{O}$ for O_2 has a reported value of 23.5‰ (Kroopnick and Craig, 1972) and the average value of $\delta^{18}\text{O}-\text{H}_2\text{O}$ -7.82 (Table 5). Using Equation 2, an estimated value of 2.62‰ is calculated for $\delta^{18}\text{O}-\text{NO}_3$. Though the $\delta^{18}\text{O}-\text{NO}_3$ does drop slightly in all the samples collected in August, they are still 10-17‰ higher than the theoretical value, so despite all the assumptions, it is unlikely that nitrification is occurring based on the $\delta^{18}\text{O}-\text{NO}_3$. The group of August samples that have more depleted $\delta^{15}\text{N}$ (0-5‰) do not seem to be of a manure mixture, rather they are likely the result of mixing with ammonium fertilizer that has started to undergo nitrification. Both fertilizers have roughly the same $\delta^{15}\text{N}$ signature, but differ greatly on the $\delta^{18}\text{O}$. If this is the case, it would mean that the vadose zone and groundwater are fairly oxygenated, allowing

plenty of oxygen for the microbes to exist without needing to strip the oxygen from the nitrate.

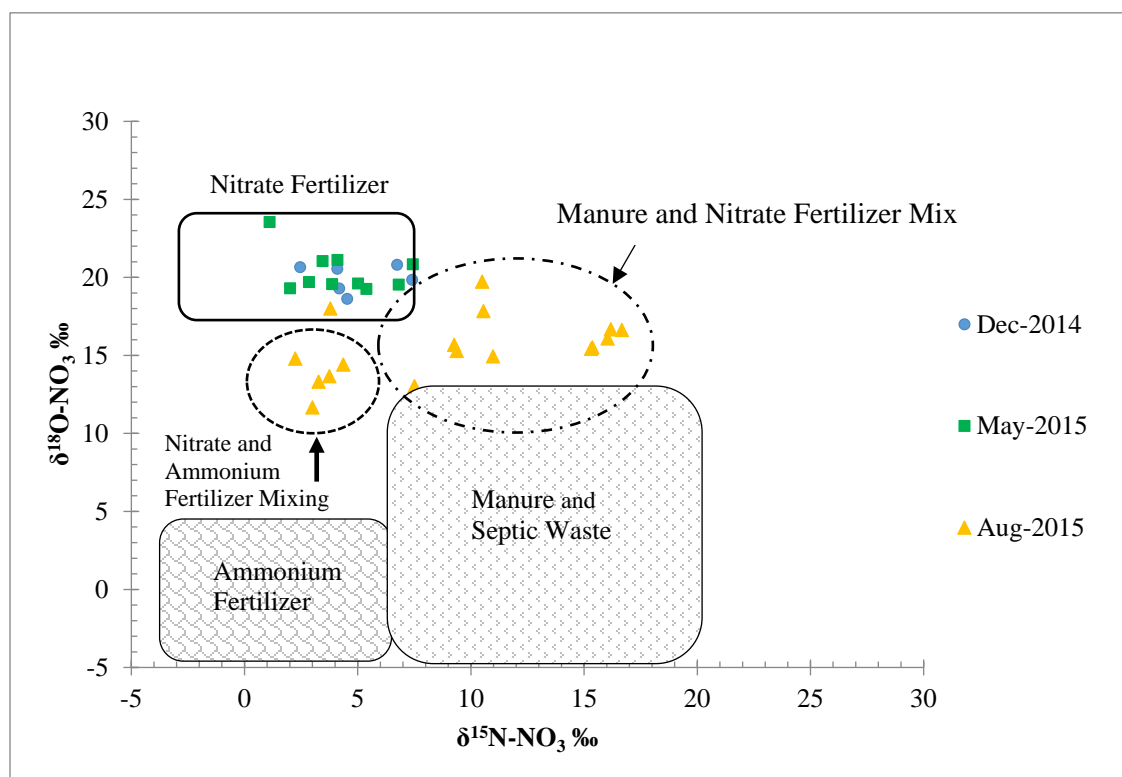


Figure 16. Dual plotting of nitrate isotopes $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ to determine nitrate sources.

Although in some cases enriched $\delta^{15}\text{N}$ values ($>10\text{‰}$) can indicate that denitrification may have affected the isotope composition, the corresponding $\delta^{18}\text{O-NO}_3$ values should also be enriched (Figure 16). Denitrification causes the $\delta^{15}\text{N}$ of the residual nitrate to increase exponentially as nitrate concentrations decrease (Kendall and Aravena, 2000). In a similar fashion, there is also an enrichment in $\delta^{18}\text{O-NO}_3$ values. In the August samples, each value of $\delta^{18}\text{O-NO}_3$ is more depleted, compared to previous months. The depletion of $\delta^{18}\text{O-NO}_3$ in many of the August samples more closely

resembles a mixture of water that has been contaminated with both synthetic nitrate fertilizer and manure. The range $\delta^{18}\text{O}$ for manure varies widely, but it is always less than the range for nitrate fertilizer.

Since mixing and denitrification can lead to similar $\delta^{15}\text{N}$ values, using the Rayleigh equation (Equation 3), which describes the evolution of the isotopic composition of the residual reactant during both kinetic and equilibrium processes (Kendall and Aravena, 2000), can lead to a better differentiation of the two processes. Using the form of the Rayleigh equation

$$\delta \approx \delta_0 + \epsilon_{p-s} \ln(f)$$

Equation 3. Rayleigh equation for systems with a constant fractionation factor

where δ_0 is the initial substrate, f is the remaining fraction of the substrate, ϵ_{p-s} is the apparent fractionation (the difference in the $\delta^{15}\text{N-NO}_3$ values measured from the field or laboratory) (Kendall and Aravena, 2000). Graphing Equation 3, $\delta^{15}\text{N-NO}_3$ is shown to become exponentially enriched as the denitrification process moves towards completion (Figure 17). The last remnant of nitrate will be highly enriched in $\delta^{15}\text{N-NO}_3$, until it has been fully converted, leaving no nitrate left to have an isotope value. The product, N_2 , is fairly depleted when the reaction begins, but will ultimately reach the same isotopic signature of the reactant (NO_3) as the beginning of the process.

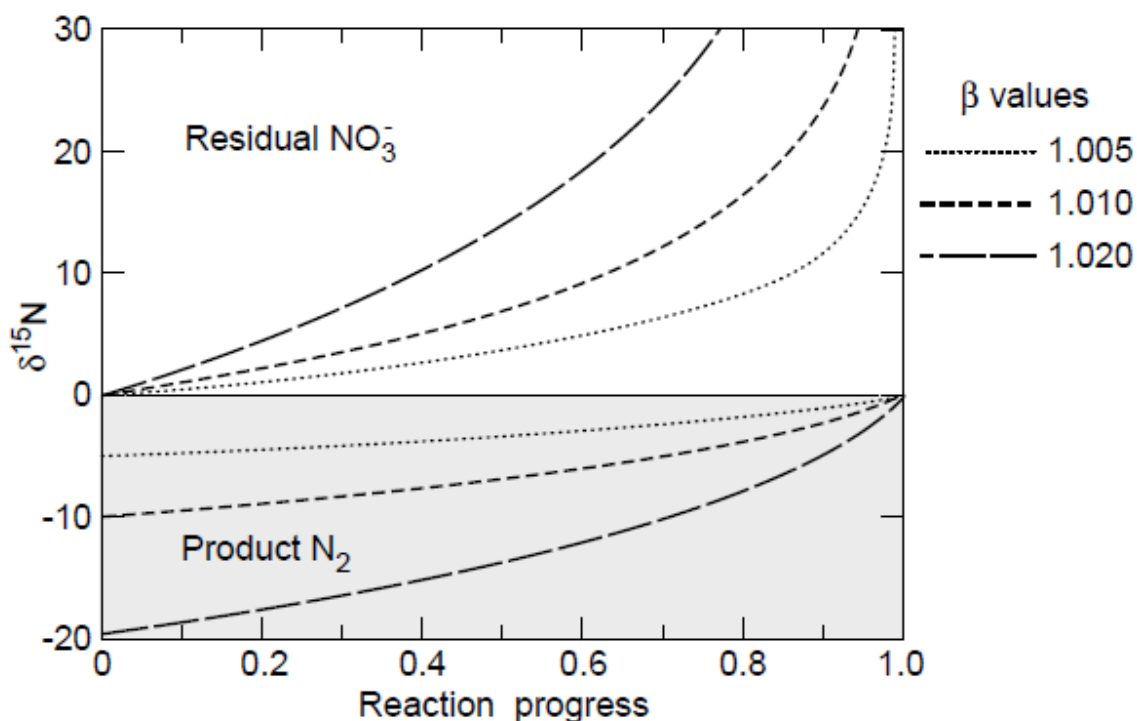


Figure 17. Reaction progress vs the $\delta^{15}\text{N}$ values of residual reactant (NO_3^-) and cumulative product (N_2) resulting from denitrification; calculated using the Rayleigh equation (Equation 3) for fractionation factors (β). Source: Kendall and Aravena, (2000)

Mariotti et al., (1988) suggests plotting the $\delta^{15}\text{N}$ - NO_3^- against nitrate concentration in two different ways to provide supporting evidence for the determination of whether mixing of denitrification has occurred. A plot of $\delta^{15}\text{N}$ vs. $1/[\text{NO}_3^-]$ yields a straight line for mixtures of two sources, and a plot of $\delta^{15}\text{N}$ vs. $\ln[\text{NO}_3^-]$ yields a straight line for any process, like denitrification, which can be described using the Rayleigh equation (Kendall and Aravena, 2000).

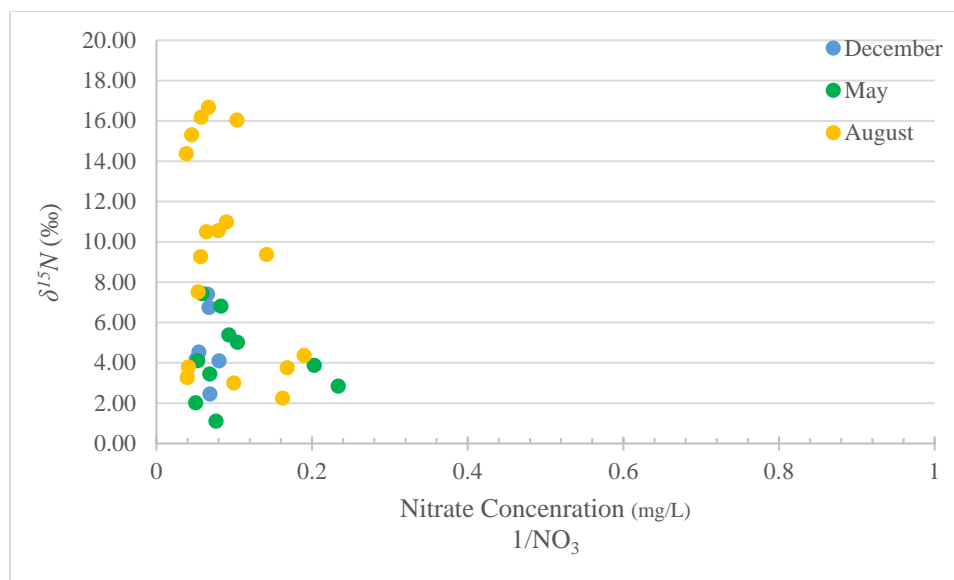


Figure 18. Plot of ^{15}N vs. $1/\text{NO}_3$ concentration to determine possible mixing of two sources of nitrate.

Figure 18 shows the distribution of values from each sampling period when plotted as $1/\text{NO}_3$. If there was mixing of two different sources of nitrate, a straight line with a negative slope would appear. Though most of the samples are in the same general range on $1/\text{NO}_3$ concentration, they do not form a line. This is likely due to having more than two sources of nitrate present. Looking at Figure 16, an argument can be made that there are at three sources present; nitrate fertilizer, ammonium fertilizer (anhydrous ammonia), and animal waste. An argument can be made that urea is also present, but it volatilizes so rapidly to form ammonia, and shares similar $\delta^{15}\text{N}$ values, that it is difficult to differentiate the two sources. The above method of source mixing determination is not viable when there are more than two sources.

Park et al., (2018) also reported seasonal variability in nitrate sources that is attributed to irrigation. During irrigation season Park et al., (2018) saw samples regulated by groundwater/soil water that were influenced by denitrification due to enhanced inputs

from irrigation return flow from irrigated rice fields. In contrast, they had other samples which was only ever influenced by $\delta^{15}\text{N}$ from manure.

Figure 19 is used to determine if denitrification is occurring in samples that have an apparent mixing of sources. Because the nitrate concentration is plotted as " $\ln(\text{NO}_3)$ ", and the process is exponential as shown using Equation 3 and in Figure 17, a straight line with a negative slope would appear if denitrification was occurring. The slope would be negative due to decreasing nitrate concentrations as it is converted to N_2 , thus enriching the $\delta^{15}\text{N}\text{-NO}_3$ in the remaining nitrate. Aside from many of the August samples having more enriched isotopic signatures, there appears to be no other trend indicating that denitrification is an ongoing process.

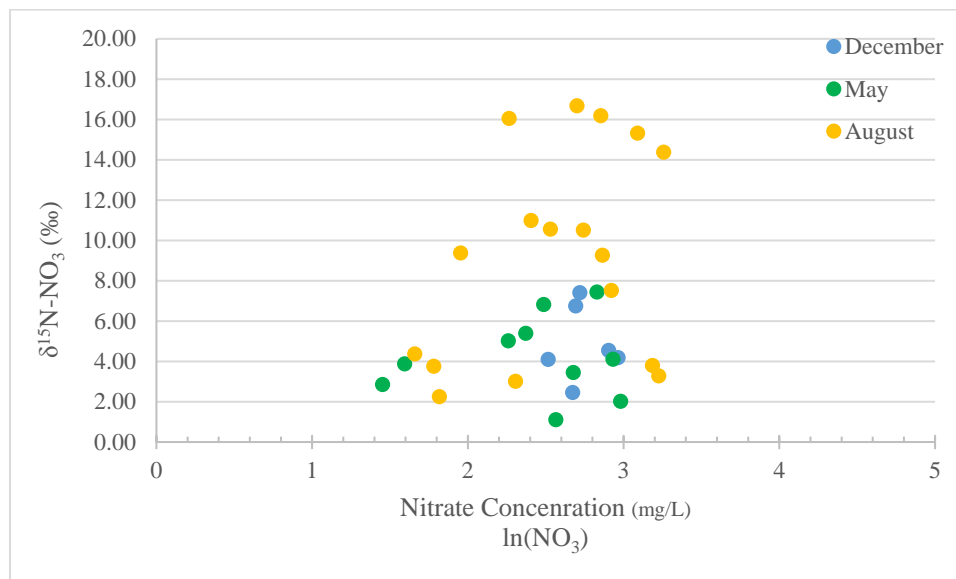


Figure 19. Plot of $\delta^{15}\text{N}\text{-NO}_3$ vs. $\ln(\text{NO}_3)$ to determine if denitrification occurring.

Though other sources of nitrate might be present, such as natural soil deposits, it is unlikely any remains after years of heavy irrigation in the region. If there are any remnant deposits of soil nitrate, the concentrations are so low that the isotopic signature is lost within the major contributors and processes present. Comparing the plotted Edgar isotope data from Figure 16 to that of Figure 3, it would seem that the section “Marine NO_3^- ” seems to be a good fit for the August data, but great distance from any coast /salt body would rule this out as a reasonable option.

5.1.3 Water Isotopes

The water isotopes are summarized in Table 5 and plotted in Figure 20 and Figure 21. When plotted by well depth, no real pattern or trend emerges, but when grouped by collection time, a slight trend appears. Samples collected from each of the three month plots are relatively uniform with respect to $\delta^{18}\text{O}\text{-H}_2\text{O}$ with an average value of -7.82‰ and a standard deviation of 0.4050‰ , but have a much wider spread with respect to δD , with an average value of -59.08‰ and a standard deviation of 6.08‰ . Bowen, et al. (2007) estimate that δD precipitation values for south central Nebraska, where Edgar is located, should be between -53‰ and -71‰ , and $\delta^{18}\text{O}$ precipitation values should fall between -7.7‰ - 8.7‰ . Their data is based on local water lines from North Platte and Mead, Nebraska. (Harvey et al., 2000; Harvey, 2001)

Most of Edgar’s samples do not fall on any of the three water lines. The samples that do fall on the line were all collected in August. That is not to say that all the samples collected in August plot in this manner. They plot most closely with the North Platte water line. Groundwater isotopes can differ slightly from the local meteoric water line due to other processes that could fractionate the groundwater isotopes, mainly

evaporation. As irrigation is applied (sprayed, drip, or flood), the water is subjugated to evaporation due to more time sitting on the land surface. When this occurs, both isotopes become enriched and deviate from the local water line that is based solely on precipitation.

Well ID	$\delta^{18}\text{O-H}_2\text{O}$			$\delta\text{D-H}_2\text{O}$		
	Dec '14	May '15	August '15	Dec '14	May '15	August '15
G-159106	-	-7.24	-7.47	-	-55.2	-56.9
G-167135	-7.61	-7.89	-7.97	-57.5	-62	-55.5
G-167136	-7.74	-7.53	-8.57	-59.1	-57.6	-52
G-167137	-7.51	-7.75	-7.58	-59.3	-58.2	-65.6
G-167138	-7.31	-7.41	-7.75	-57.7	-56.8	-53.3
G-167139	-7.69	-7.66	-7.89	-55.3	-55.5	-58.1
G-167140	-7.38	-7.43	-7.39	-70.5	-56.2	-47.8
G-175919	-	-8.22	-8.79	-	-71	-72.6
G-175925	-	-8.02	-8.61	-	-66.7	-66.7
DW-1	-	-7.55	-7.37	-	-58.4	-59
DW-2	-	-	-8.18	-	-	-54.6
DW-3	-	-	-7.85	-	-	-55.6
Municipal	-	-	-8.04	-	-	-54.7
DW-4	-	-	-8.46	-	-	-66.2
DW-5	-	-	-7.63	-	-	-61.3
DW-6	-	-	-8.14	-	-	-57.9
DW-7	-	-	-8.36	-	-	-55

Table 5. Edgar groundwater δD and $\delta^{18}\text{O}$ isotopic values

One issue with direct comparison of meteoric water lines and groundwater samples is that in cases such as in Edgar, where irrigation is so prevalent, it is quite possible that the same water could be used multiple times. When precipitation reaches the water table with expected isotopic ratios for the area (elevation, season, and position on the continental mass) the water could be drawn into an irrigation well and applied to a

field. When this occurs, further fractionation occurs as the water is sprayed into the air and then allowed to sit on the land surface evaporating, causing further fractionation and enrichment of both $\delta^{18}\text{O}\text{-H}_2\text{O}$ and δD as the lighter isotopes are preferentially evaporated.

As water infiltrates and moves past the root zone and reaches the water table, the cycle occurs again. Even in areas where irrigation is not widespread, groundwater tends to be depleted with respect to VSMOW $\delta^{18}\text{O}\text{-H}_2\text{O}$ and δD because of the extra fractionation that occurs while infiltrating into the groundwater. Park et al., (2018) reported similar seasonal variance in both $\delta^{18}\text{O}\text{-H}_2\text{O}$ and δD in both shallow and deep wells and attributed it to a mixing of seasonal precipitation mixing followed closely by irrigated water that has been subjected to evaporation from sitting on the land surface.

Evaporation is occurring at a high rate meaning the ambient air temperature is warm enough to drive the process. The notable isotopic change in $\delta^{18}\text{O}\text{-H}_2\text{O}$ and δD for the August samples gives merit to the theory that water being pumped later in the year is from a mixture of different waters. Since widespread irrigation has been a seasonal event for the latter half of the previous century, it is plausible that water is not reaching the deeper portions of the aquifer where some of the wells are screened. Samples collected in December and May may reflect more natural water isotopic values and are mixing with water that has been used for irrigation one more than one occasion. If this is the case, it might explain why the δD values are slightly enriched.

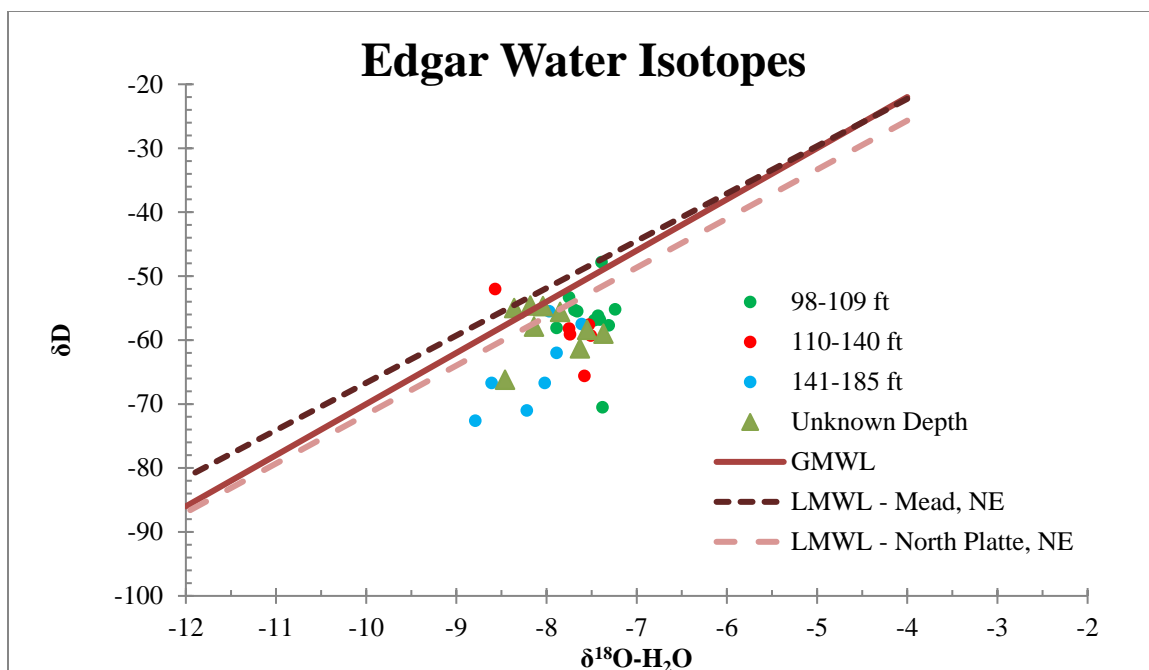


Figure 20. Edgar Water Isotopes. Graphed by sampling depth. GMWL represent Global Meteoric Water Line. LMWL represents Local Meteoric Water Line

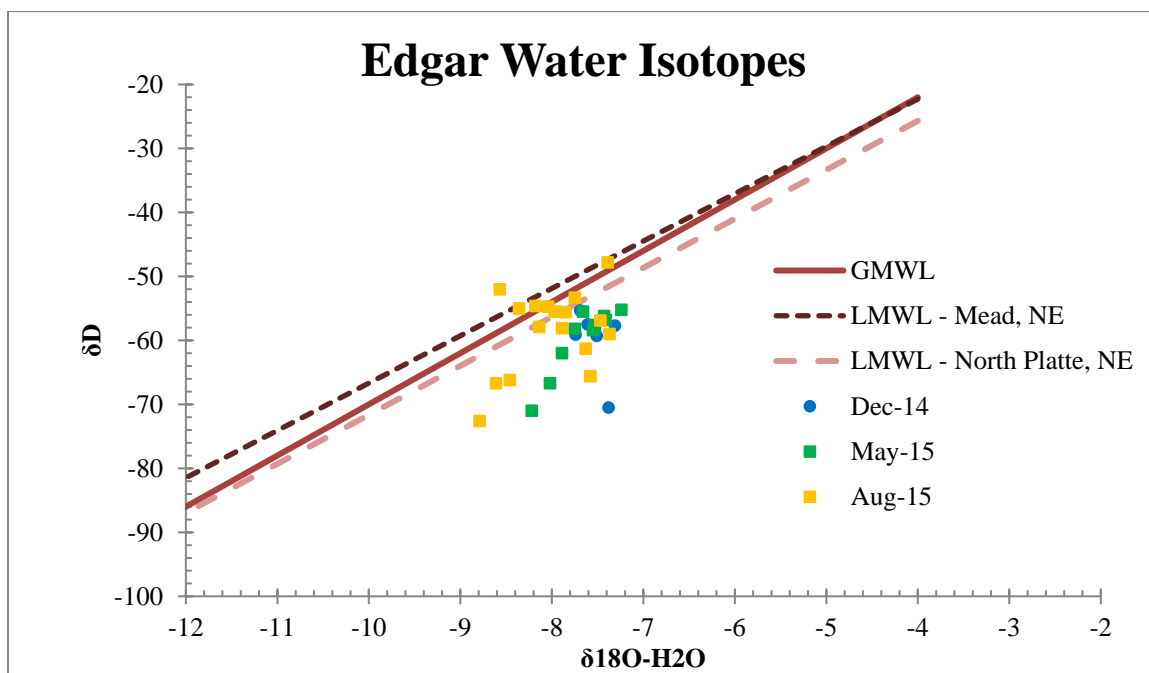


Figure 21. Edgar Water Isotopes. Graphed by sample collection date. GMWL represent Global Meteoric Water Line. LMWL represents Local Meteoric Water Line

5.1.4 Major Ions and Trace Metals

Major ions were investigated to get a look at the groundwater chemistry and help determine nitrate sources. Table 6 and Table 7 show ion concentrations from each sample. There is consistently little bromide, fluoride, or phosphate found in any of the samples. Sulfate shows fairly consistent results with an average value of 35.84 mg/L, but does slightly decrease in the August samples. Chloride concentrations were also consistent with averages differing by only 1.56 mg/L, but again show a slight decrease in August. There was an anomalous concentration of 35.55 mg/L which can be indicative of a septic tank leak, but the sodium concentration, which would also be expected to be higher based on salty human diet and added water softeners, was towards the low side of measured concentrations. Only a few samples were analyzed for alkalinity (HCO_3^-), of the samples analyzed, HCO_3^- was much higher in concentration than all the other anions combined. Even if there are fluctuations in the concentrations from different parts of the year, an average value 348.71 mg/L, bicarbonate is likely to be the major anion contributor year round.

Calcium and sodium are the two major cation contributors, calcium the bigger of the two. In December and May, each of the two ions are comparable to the other and generally follow the same trend, if calcium is relatively high, then sodium is also, if calcium is lower, then so is sodium with averages of calcium and sodium being 50.13 mg/L and 51.10 mg/L respectively Figure 22 and Figure 23. August samples break the trend. With the exception of wells, G-167138, G-167139, and G-167140, sodium levels drop dramatically. Calcium concentrations on the other hand, increase substantially in August. There are several domestic wells that were only sampled in August that have

high concentrations, that might skew the results, but other wells that were sampled in December and May also show large increases in concentration. The positive shift in concentration also occurs with potassium and magnesium, though not as drastic.

Magnesium saw a small increase of 3.3 mg/L on average, and potassium saw an average increase of 1.21 mg/L (Figure 22 and Figure 23). These changes are relatively small, but the fact that every sample saw an increase speaks to the fact that there appears to be a difference in the water being pumped.

Well ID	Calcium (mg/L)			Magnesium (mg/L)			Sodium (mg/L)			Potassium (mg/L)		
	Dec '14	May '15	August '15	Dec '14	May '15	August '15	Dec '14	May '15	August '15	Dec '14	May '15	August '15
G-159106	-	61.25	70.89	-	13.92	16.73	-	43.02	29.56	-	4.39	5.58
G-167135	50.16	46.64	80.57	14.35	12.88	19.93	49.88	47.68	28.60	4.17	4.21	5.27
G-167136	46.86	50.40	98.45	14.80	14.23	19.04	37.70	45.34	27.85	3.96	4.40	5.63
G-167137	44.90	51.65	83.42	14.00	12.53	16.99	68.40	67.16	31.50	3.75	4.14	4.18
G-167138	55.21	60.97	99.29	11.18	13.51	17.85	57.40	62.44	76.65	4.06	4.30	5.18
G-167139	49.78	50.87	82.20	14.20	13.06	16.05	72.34	69.80	75.25	4.22	4.26	5.26
G-167140	42.46	52.49	83.91	14.90	13.53	16.14	52.19	51.98	54.40	4.25	4.29	5.08
G-175919	-	29.35	43.75	-	10.37	12.41	-	29.26	22.90	-	3.23	4.93
G-175925	-	34.89	57.47	-	10.08	14.08	-	25.53	23.25	-	3.53	5.78
DW-1	-	74.26	104.08	-	15.41	18.34	-	37.53	31.35	-	4.25	4.85
DW-2	-	-	80.63	-	-	15.53	-	-	24.65	-	-	3.32
DW-3	-	-	73.91	-	-	14.97	-	-	35.80	-	-	4.70
Municipal	-	-	72.39	-	-	16.26	-	-	23.95	-	-	3.72
DW-4	-	-	55.08	-	-	13.45	-	-	17.35	-	-	5.70
DW-5	-	-	107.04	-	-	19.60	-	-	46.40	-	-	7.28
DW-6	-	-	76.06	-	-	16.13	-	-	24.15	-	-	6.49
DW-7	-	-	91.02	-	-	18.90	-	-	44.50	-	-	7.13

Table 6. Major Cations in groundwater beneath Edgar

Well ID	Fluoride (mg/L)			Chloride (mg/L)			Phosphate (mg/L)			Sulfate (mg/L)			Bicarbonate (mg/L)		
	Dec '14	May '15	August '15	Dec '14	May '15	August '15	Dec '14	May '15	August '15	Dec '14	May '15	August '15	Dec '14	May '15	August '15
G-159106	-	0.15	0.14	-	29.29	24.43	-	0.10	0.08	-	37.73	36.51	-	-	-
G-167135	0.16	0.25	0.12	22.44	20.63	21.90	0.16	0.06	0.03	45.71	47.94	43.95	-	-	-
G-167136	0.14	0.23	0.11	22.37	22.58	21.31	0.04	0.04	0.02	40.20	44.26	37.22	-	-	-
G-167137	0.16	0.14	0.13	22.83	23.36	22.18	0.03	0.05	0.03	41.84	38.06	40.16	-	-	-
G-167138	0.17	0.18	0.14	21.27	24.26	23.76	0.03	0.08	0.02	35.32	38.95	39.53	-	-	-
G-167139	0.18	0.17	0.14	21.30	21.69	19.10	0.06	0.17	0.03	36.29	39.08	36.78	-	364.69	-
G-167140	0.16	0.19	0.15	25.57	25.02	21.79	0.05	0.10	0.00	29.96	29.77	32.87	-	363.46	-
G-175919	-	0.25	0.21	-	15.69	16.55	-	0.07	0.02	-	28.98	29.70	-	394.48	-
G-175925	-	0.21	0.18	-	17.10	17.50	-	0.08	0.00	-	28.46	29.70	-	289.01	-
DW-1	-	0.18	0.14	-	29.80	19.63	-	0.07	0.06	-	40.32	38.64	-	331.91	-
DW-2	-	-	0.13	-	-	22.70	-	-	0.00	-	-	30.15	-	-	-
DW-3	-	-	0.14	-	-	18.11	-	-	0.00	-	-	34.86	-	-	-
Municipal	-	-	0.16	-	-	35.55	-	-	0.03	-	-	30.26	-	-	-
DW-4	-	-	0.13	-	-	18.69	-	-	0.03	-	-	27.15	-	-	-
DW-5	-	-	0.15	-	-	20.70	-	-	0.03	-	-	37.67	-	-	-
DW-6	-	-	0.15	-	-	22.66	-	-	0.04	-	-	29.66	-	-	-
DW-7	-	-	0.20	-	-	14.94	-	-	0.03	-	-	25.14	-	-	-

Table 7. Major anions in the groundwater beneath Edgar

Looking at the composition of all the ions together, the source waters appear to be mostly of Ca-Na-HCO₃ during December and May, but in August, switches to a mostly Ca-HCO₃ water that is expected for groundwater in the area. Fillmore county (one county to the east) is known to have waters of similar composition (Gosselin et al., 2001). This is further evidence of mixing of water in samples collected in August. Wells located near the water table, or near an irrigation well tend to see changes in water chemistry, whereas wells G-175919 and G-175925 showed consistently lower concentrations in every major ion analyzed in every sampling event. This trend is also seen with the nitrate concentrations and isotopes from sections 5.1.1 and 5.1.2.

The data was entered in the program PHREEQC to determine solubilities and saturation indices of possible minerals that could be formed from the ions measured. There are no minerals that are saturated, but calcite (calcium carbonate) and its polymorph, aragonite are nearly saturated, in five of the samples where alkalinity was measured. Other minerals such as dolomite (calcium magnesium carbonate), fluorite (calcium fluoride), gypsum (calcium sulfate dihydrate), and anhydrite (calcium sulfate) are all generally the same extent of undersaturated, being slightly more undersaturated than calcite and aragonite. Halite (sodium chloride) and sylvite (potassium chloride) are both the most undersaturated in each sample.

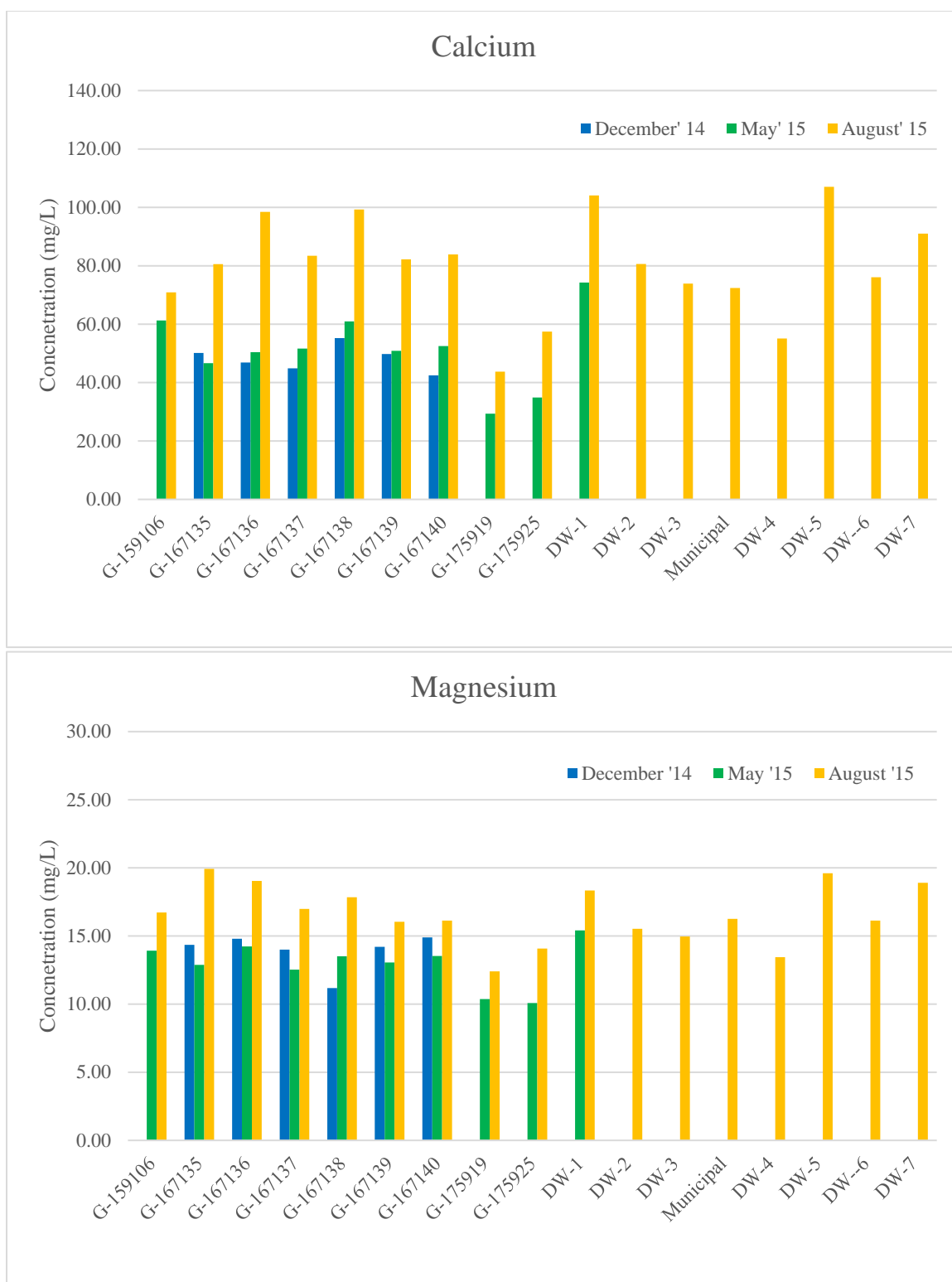


Figure 22. Calcium and magnesium concentrations from each sampling period.

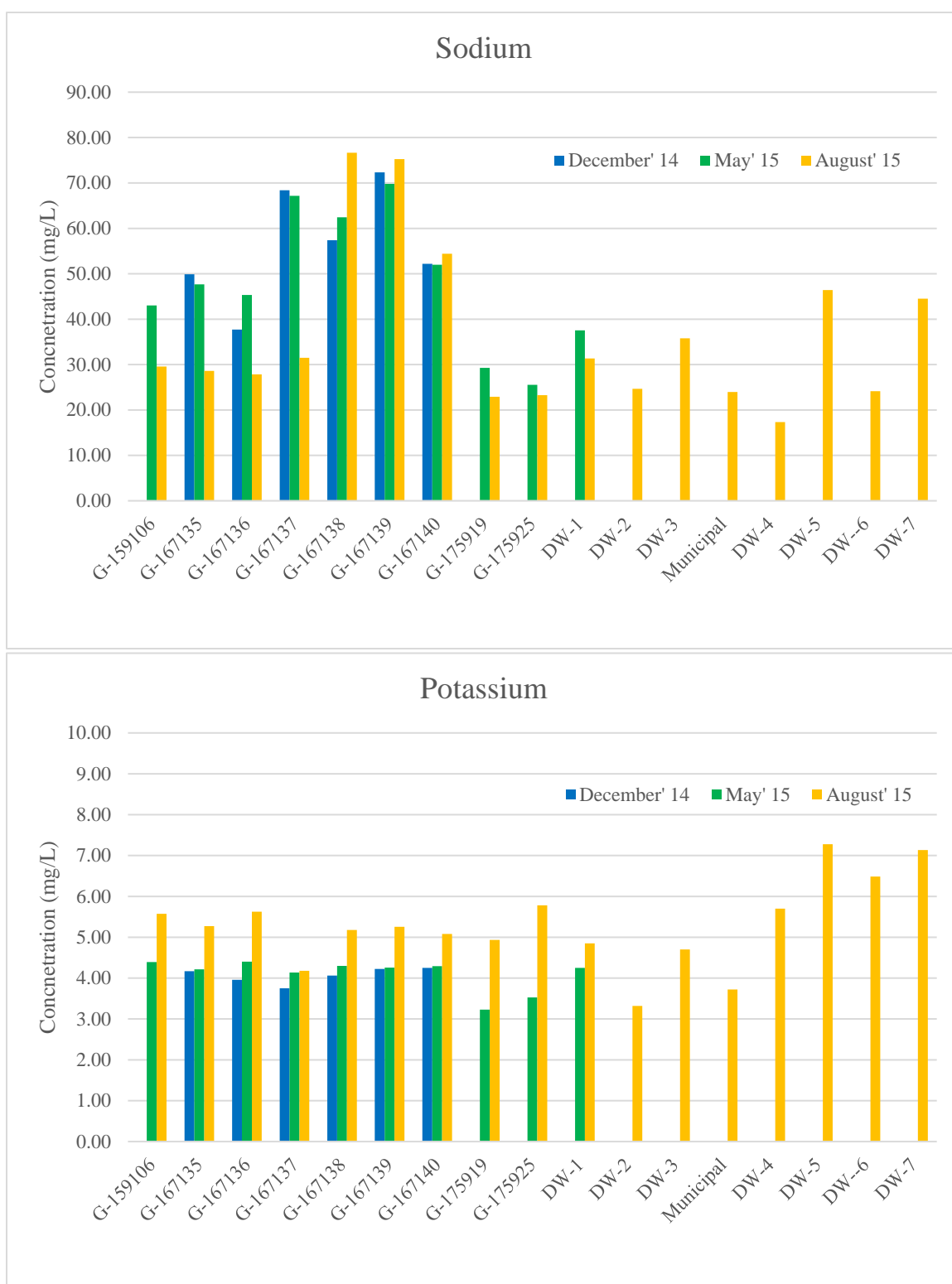


Figure 23. Sodium and potassium concentrations from each sampling period.

Trace Metals

Uranium and selenium concentrations were below the MCL (30 µg/L and 50 µg/L respectively) for each sample. With average values of 3.17 µg/L for uranium and 7.85 µg/L for selenium, the groundwater in this area is relatively clean with regard to these two trace metals. Unlike their neighbor upgradient, these results indicate that there are likely no natural deposits of either metal in any real quantity located in the WHPA or immediately outside the WHPA. Interestingly though, the same trend was found in all but one of the samples that were samples more than once. Except for well G-167137, each site showed increased concentration for uranium during each sampling period. The concentration of selenium was much more consistent from the three sampling periods, but a slight trend can be teased showing that seven of the nine sites that were sampled more than once had elevated concentrations in August.

6.1 Conclusion and Future Direction

An apparent seasonality exists in the groundwater quality below Edgar that can be linked to historical and current land use and caused by seasonal effect of irrigation. Nitrate sources and concentrations are not uniform throughout the groundwater beneath Edgar. Evidence to this claim can be seen in nitrate concentration and isotopic signatures, in water isotopic signatures, and in major ion and trace metal concentrations. It is likely that the seasonality is caused by the extensive irrigation both inside and outside the WHPA. The drawdown created by the large irrigation and municipal wells, causes water that is located closer to the surface to be drawn down and mixed with deeper and older waters. In addition, there are likely multiple sources of nitrate that are effecting the quality of water at different times of the year. In the winter and spring months, the likely culprit of contamination is from synthetic nitrate fertilizer, but toward the end of the summer, a mixture of several different sources occurs, including synthetic nitrate fertilizer, manure (animal waste), and microbial nitrification. Point and non-point sources both play a role in the overall nitrate contamination of groundwater. The general application of fertilizers to fields, as well as abandoned and active livestock enclosures are to blame for the current situation.

Changes in hydrogeochemistry also suggests that water mixes to a greater degree after irrigation wells have been pumping on and off for four or five months. Most of the samples were notably and consistently higher with respect to magnesium, calcium, potassium, and uranium in the August dataset, indicating the water was of a different source.

The deep groundwater that is much less affected by irrigation is lower in nitrate concentrations and has similar isotopic signatures throughout the year. A shift in isotopic ratios to the degree that was discovered in Edgar is not common, so repetition of the sampling should be carried out, with perhaps more wells sampled during multiple times throughout the year to see if the same pattern presents itself. This would be useful to ensure the phenomenon did not occur solely in the sample collection time frame of this project.

This project, funded by the Village of Edgar (with a grant from Nebraska Department of Environmental Quality), will also include water age dating using the $^3\text{H}/^3\text{He}$ method to determine the age of the groundwater being used by the city's municipal wells. Conducting this analysis could help to support seasonal mixing of groundwater reported here by determining if the water collected in August was younger (more recently recharged) than the water collected in December or May.

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