Bazile Ground Water Management Area Isotope and Recharge Study

Final Project Report

Daniel D. Snow, Laboratory Director
Water Sciences Laboratory
Nebraska Water Center
University of Nebraska
**Lincoln, NE 68580-0844**

and

Daniel N. Miller, Research Microbiologist
USDA-ARS, Agroecosystem Management Research Unit
354 Filley Hall, UNL East Campus
Lincoln, NE 68583-0937

March 30, 2018

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Introduction

The Bazile Groundwater Management Area (BGMA) covers 756 square miles within Antelope, Knox, and Pierce counties in Northeast Nebraska and includes regions within the Lewis and Clark, Lower Elkhorn, Lower Niobrara, and Upper Elkhorn Natural Resource Districts. Aquifers within this area supply drinking water to ten rural communities and several thousand residents. Nitrate contamination has affected municipal wells in the vicinity of Brunswick, Creighton, Orchard, Osmond, Plainview, Royal, and Wausa Nebraska (figure 1). Previous and ongoing investigations have collected data and information to help understand the nitrogen sources and causes for nitrate contamination which appears to be increasing in several parts of this region. A recent study of nitrate contamination in eastern Nebraska (Exner, Hirsh et al. 2014) describes the landscape as excessively well-drained soils with a highly permeable unsaturated zone with a relatively high density of sprinkler or center pivot irrigation. Subsurface geological reports suggest heterogeneously distributed layers of aeolian sand, with alluvial sands, silts with little evidence for continuous clays. Currently it is thought that these soils and unsaturated zone sediments are highly vulnerable to excess nitrate formation and leaching from any source, with little potential to reduce lost nitrate via denitrification. The Ogallala aquifer, located beneath this management area, has a saturated thickness reaching 150 meters (Souders 1969). Elevated nitrate concentrations occur at depth beneath the water table suggesting that vertical mixing within the aquifer may be the result of high pumping rates and/or gravel packed annular spaces of the densely distributed
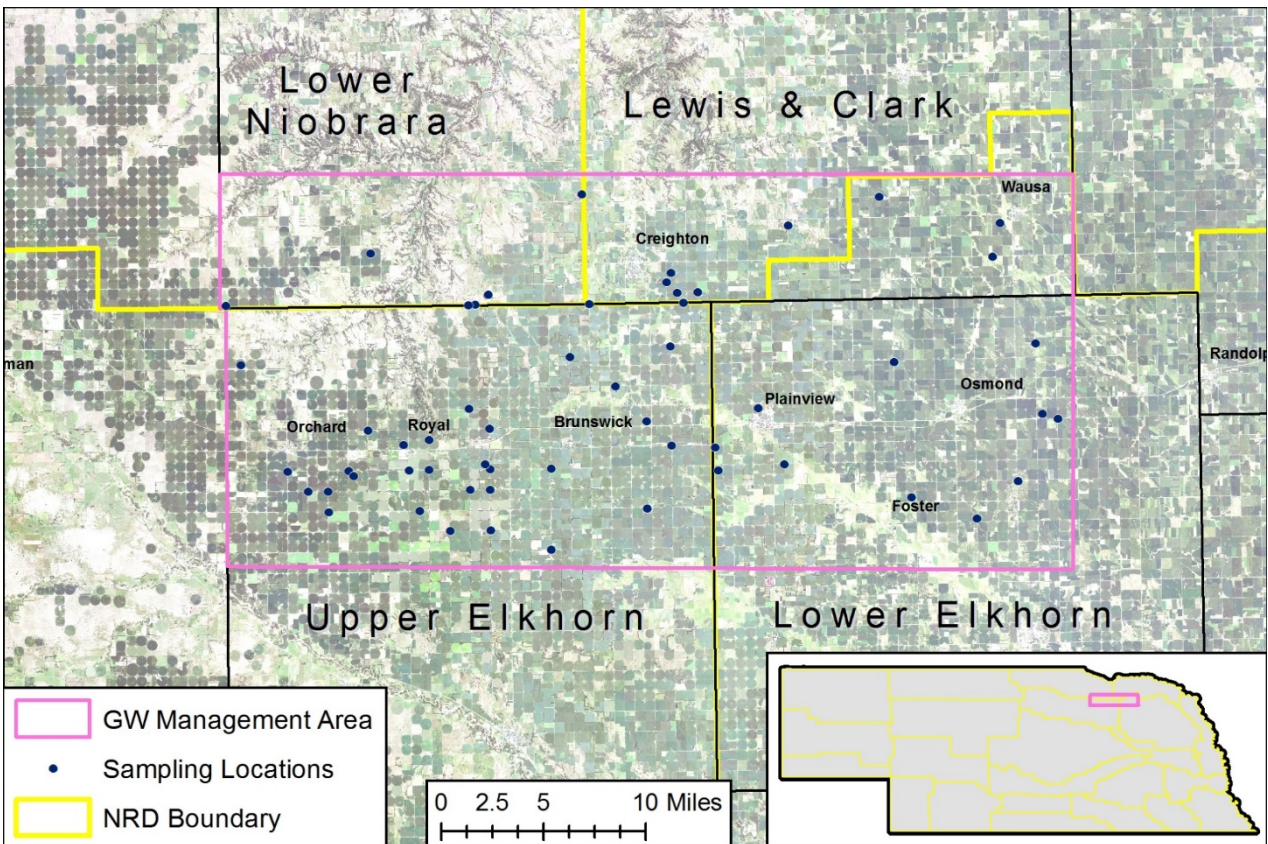
Figure 1. Map of the Bazile Groundwater Management Area showing the locations of the wells sampled for isotope analysis.

irrigation wells (Spalding, Watts et al. 2001, Exner, Hirsh et al. 2014). The areal extent of nitrate contamination in the aquifer has been growing over the past several decades at a rate of approximately 18,600 ha/yr (Exner, Hirsh et al. 2014).

Groundwater management plans have been implemented in each natural resource district included in the BGWA, however it is generally recognized that even drastic changes in fertilizer and irrigation practices at the surface will be slow to impact nitrate levels in the aquifers. Recharge rates likely vary across the area and temporally due to soil types, topography, depth to water, irrigation practices and seasonal rainfall amounts. Nitrate contamination at a specific location may be the result of excess nitrogen application and nitrate leaching years or even decades ago. Because some uncertainly exists with respect to the historical sources of excess nitrogen leading to nitrate contamination at a given location, there can be a reluctance to follow recommended practices to reduce nitrogen loading at the surface. Though most previous studies of the area (Exner, Hirsh, et al., 2014, Exner and Spalding, 1979, Exner and Spalding, 1991) have indicated that the majority of the excess nitrogen has been applied in the form of commercial fertilizer, some locations may also be influenced by application of nitrogen from animal manure. High nitrate coupled to bacteria contamination at some locations have also suggested that improperly constructed wells, particularly those in farmyards and susceptible to run-off, may have also contributed to point sources of nitrate in this region (Gosselin, Headrick et al. 1997). Whatever the sources, nitrogen management practices will have the greatest impact if applied with the best available information on what locations are most vulnerable and which areas a less prone to nitrate formation and leaching.

Forms of Nitrogen
Multiple forms and sources of nitrogen contribute to the occurrence of excess nitrate in soils and the unsaturated zone. In routine soil tests, nitrate-N alone is usually measured, though significant amounts of other forms of N are ammonium and organic nitrogen. Soil ammonium comes from urea, ammonia, and manure application or from the breakdown of organic nitrogen (crop residues and manure). Normally ammonium binds tightly to soil and moves very slowly, however, microbial processes continuously convert organic N to ammonium to nitrite and nitrate (the process of nitrification). This 'bank' of nitrogen in the soil and unsaturated zone is easily built up by fertilizer application (even at recommended rates) and has the capacity to release nitrate over many years. As demonstrated in previous work, over application of irrigation water has the unfortunate side effect of leaching nitrates down below the crop root zone (Spalding, Watts et al. 2001). Increasing nitrate concentrations in groundwater are generally linked to fertilizer and/or organic nitrogen (e.g. animal manure) applied in excess of crop requirements. Over application of any of nitrogen source can result in high soil nitrate and subsequent nitrate leaching. Once in the unsaturated zone, excess nitrate will eventually be transported to the water table unless there exists a potential for nitrate reduction through denitrification.

Nitrate Isotope Analysis
Nitrate is composed of both nitrogen and oxygen, while ammonium is composed of nitrogen with hydrogen. Nitrogen has two natural stable isotopes while oxygen has three. The composition or proportion of these isotopes changes in a predictable way. Nitrogen in commercial fertilizers (urea and anhydrous ammonia) has an isotope composition very similar to atmospheric nitrogen, and typically ranges from -5 to +5 per mil (‰). Nitrogen from animal manure, sewage or biosolids tends to be enriched in the heavier ^{15}N isotope, especially after deposition and conversion to the highly volatile ammonia (Kendall, Elliott et al. 2008). In comparison to commercial fertilizer (figure 2), nitrogen isotopes of nitrogen from livestock manure and septic systems tend to range between +5 to +25 ‰. When nitrogen from any of these sources is converted to nitrate, it carries with it a signature of the original 15N isotope composition.

Oxygen isotopes in nitrate, on the other hand, come from oxygen in the soil air and water. Because the oxygen isotope composition in air is relatively constant (+22 to +24‰), and the oxygen isotope composition of water changes in a predictable way (usually -5 to -20‰), it is possible to use the oxygen isotope composition of soil nitrate to determine when nitrate was formed. Both the nitrogen and oxygen isotope composition are affected by another process called microbial denitrification, which can also change nitrate to nitrogen gas and water. Because the change in composition is predictable, simultaneous measurement of both nitrogen and oxygen isotopes can provide clues about the source(s) of nitrogen, timing of nitrification (nitrate formation), and whether denitrification has helped to remove any nitrate. As figure 2 indicates, however, the use of both nitrogen and oxygen isotopes for distinguishing sources of nitrate in groundwater can be complicated by multiple sources (atmospheric, manure, septic systems) and processes.
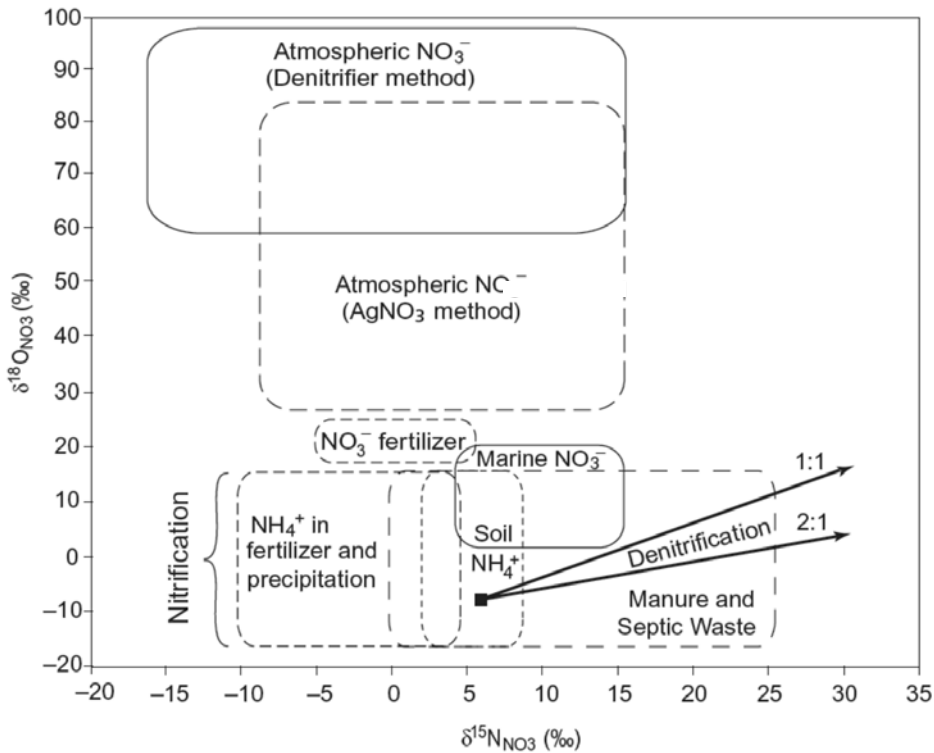

Figure 2. Expected variation of ^{15}N-NO$_3$ and ^{18}O-NO$_3$ from a variety of sources, along with the predicted trends due to denitrification (Kendall et al 2008).

Site Locations and Sample Collection
This study sampled wells from 52 locations across the Bazile GWMA for nitrogen concentration an isotopic composition in the fall 2015 and summer 2016 (Figure 1). An additional 11 samples were collected in 2017 for dissolved gases, age-dating and isotope analysis. Historically, 26 of these locations were previously sampled for ^{15}N in 2000 (Burbach and Spalding, 2001). The other locations were selected based on their changing nitrate concentrations or location within a wellhead protection area. Ground water samples for nitrate isotope were collected in 1-liter polyethylene bottles, transported on ice and frozen within 24 hours of collection. The methods used for measurement are described at the end of this report.

Results

Nitrate-N concentrations from wells within the Bazile Groundwater Management Area average 15.6±8.5 mg/L and two of the wells sampled in 2015 had insufficient nitrate-N for isotope analysis. The ^{15}N composition of 72 of the 74 samples averaged 1.9 ±2.3 per mil ($^o/_{oo}$) relative to atmospheric nitrogen (figure 3) and was not correlated to nitrate concentration. The range of ^{15}N -NO$_3$ in these samples is comparable to those reported previously from the Creighton, Nebraska area (Burbach and Spalding, 2001) and the average is actually more characteristic of nitrate-N from commercial fertilizers. The highest value (+8.0 per mil) is nearly identical to the highest value reported in the Creighton groundwater study, with a
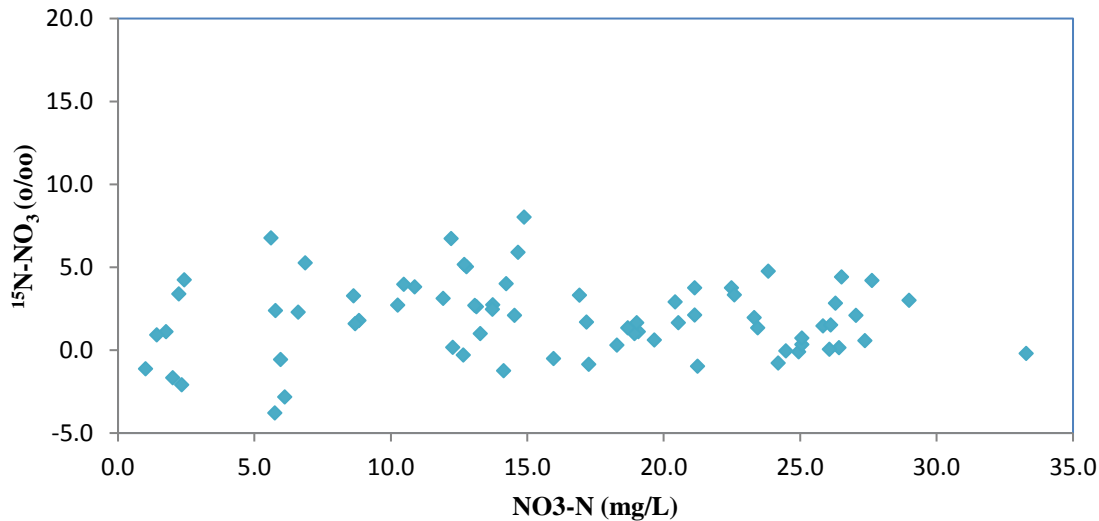
Figure 3. Variation of ^{15}N-NO$_3$ composition (per mil) versus nitrate-N concentration (mg/L) for all samples collected between 2015 and 2017. The average ^{15}N-NO3 is +1.9±2.3 per mil and there is no trend between nitrate-N concentration and ^{15}N composition.
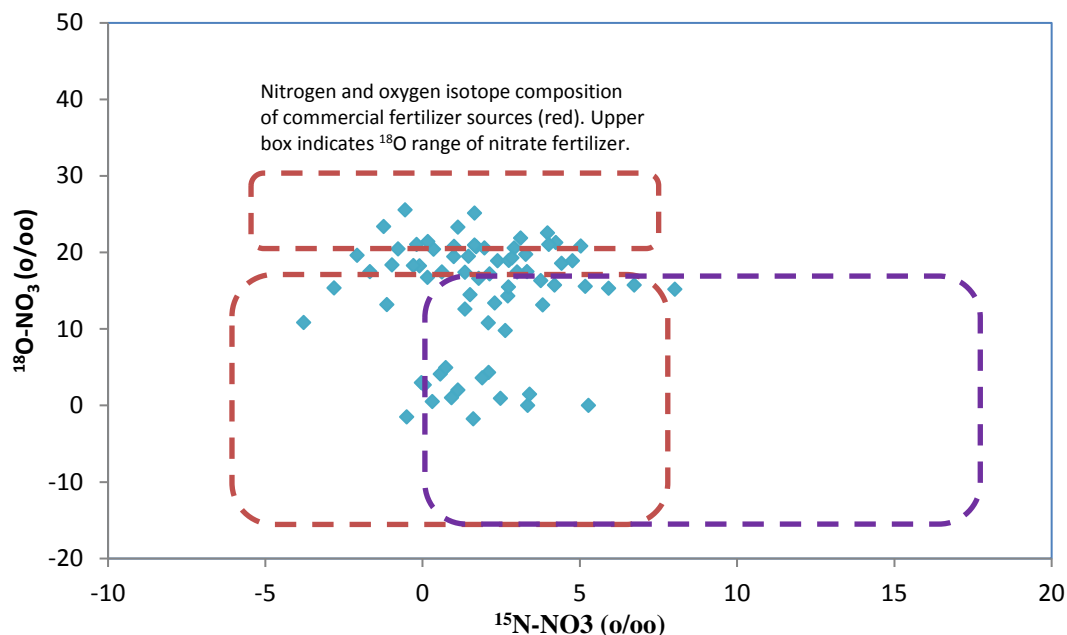
Figure 4. Comparison of ^{18}O-NO$_3$ composition (per mil) versus ^{15}N-NO3 of nitrate (per mil) in samples collected from the Bazile Groundwater Management Area compared to ranges expected in commercial inorganic (red boxes) fertilizer and organic nitrogen source (purple box) sources based on the review by Kendall et al 2008.

postulated organic nitrogen source. As illustrated in figure 2, there is some overlap in ^{15}N-NO_3 isotope values of nitrate for commercial fertilizer and organic sources between +1 and +5 per mil. In other words, the ^{15}N-NO_3 composition is not a good indicator of source in this range.

The oxygen isotope composition (^{18}O) of nitrate the samples averaged +15.1 ±7.1 per mil relative to seawater oxygen standard (Figure 4). Overall, the ranges for both ^{15}N and ^{18}O-NO_3 suggests that the majority of the samples are consistent with nitrate-nitrogen derived from commercial fertilizer (-10 to +5 per mil or a mixed source (+2 to +8 per mil). Overall the ^{18}O-NO_3 of nitrate is consistent with nitrification of applied nitrogen fertilizer, either from commercial sources or applied livestock manure and about 20% exhibit an oxygen isotope composition characteristic of nitrate fertilizer. In summary, isotopic analysis of groundwater nitrate support chemical fertilizers as the main source of groundwater nitrate though some areas may reflect nitrogen from an organic source.

**Processes controlling groundwater nitrate-N**
Assuming a uniform accumulation and loading of nitrate-N from fertilizer application near the surface, topography and thickness of the unsaturated zone, along with recharge rates will control leaching to the water table. All other factors being equal, and assuming uniform fertilizer application, areas with more rapid nitrate leaching will likely occur where soils are well drained and distance to water is less. The map in figure 5 shows the estimated thickness of the vadose zone using static water levels reported for the monitoring wells sampled in this project. In general, depth to water is greatest in the northeast corner of the Bazile Groundwater Management Area and lowest in the river valleys running through northwest to southeast across the region.

A comparison of the estimated distance to the water table to the spatial distribution of nitrate-N concentrations is shown in Figure 6. Though this map is based on a relatively limited dataset, lower concentrations are generally observed in the northeast corner of the area and higher concentrations occur in the southwestern region and along the river valleys. It is interesting to note that the general distribution of vadose zone thickness happens to coincide with a zone of higher recharge modeled using evapotranspiration Calibration-Free Evapotranspiration Mapping (CREMAP) model (Szlagi and Josza,
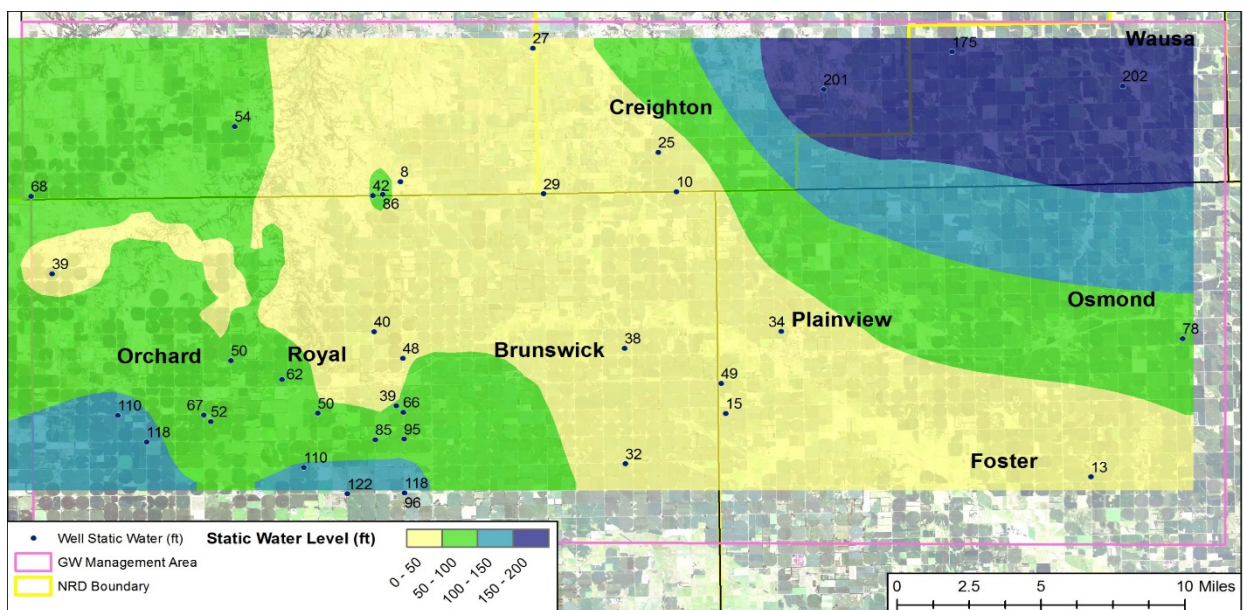
Figure 5. Spatial variation of thickness of the vadose zone estimated using depth to static water levels from monitoring wells sampled for this project.
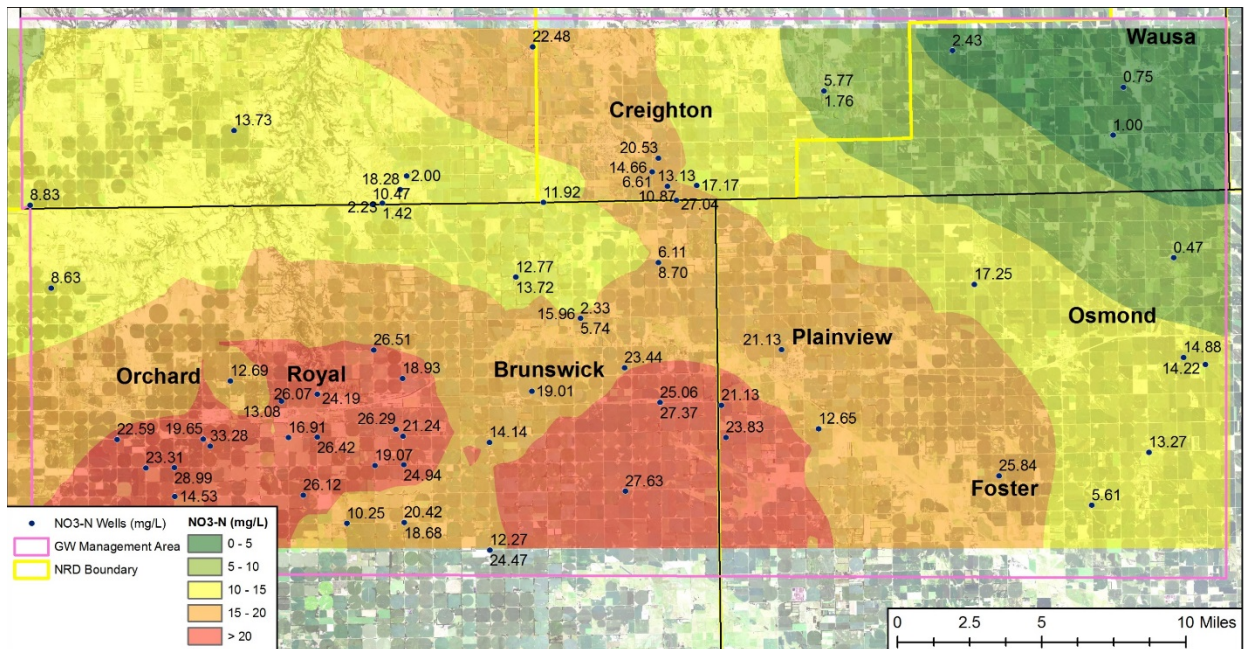
Figure 6. Spatial distribution of nitrate-N concentrations from monitoring wells used in this study interpolated using ARCGIS.

2013). The estimated groundwater ages from helium-tritium analysis will help evaluate where "hotspots" exist and where changing surface management will most rapid effect in the subsurface.

A map showing the spatial distribution of ^{15}N-NO$_3$ (figure 7) generally indicates a uniform isotope composition of nitrate, regardless of depth to water or nitrate concentration. The lack of a pattern or ^{15}N-NO$_3$ "plume" suggests that the source is relatively uniform and generally unaffected by denitrification. Nitrate from manure or livestock wastewater lagoon leakage has occasionally been observed to result in
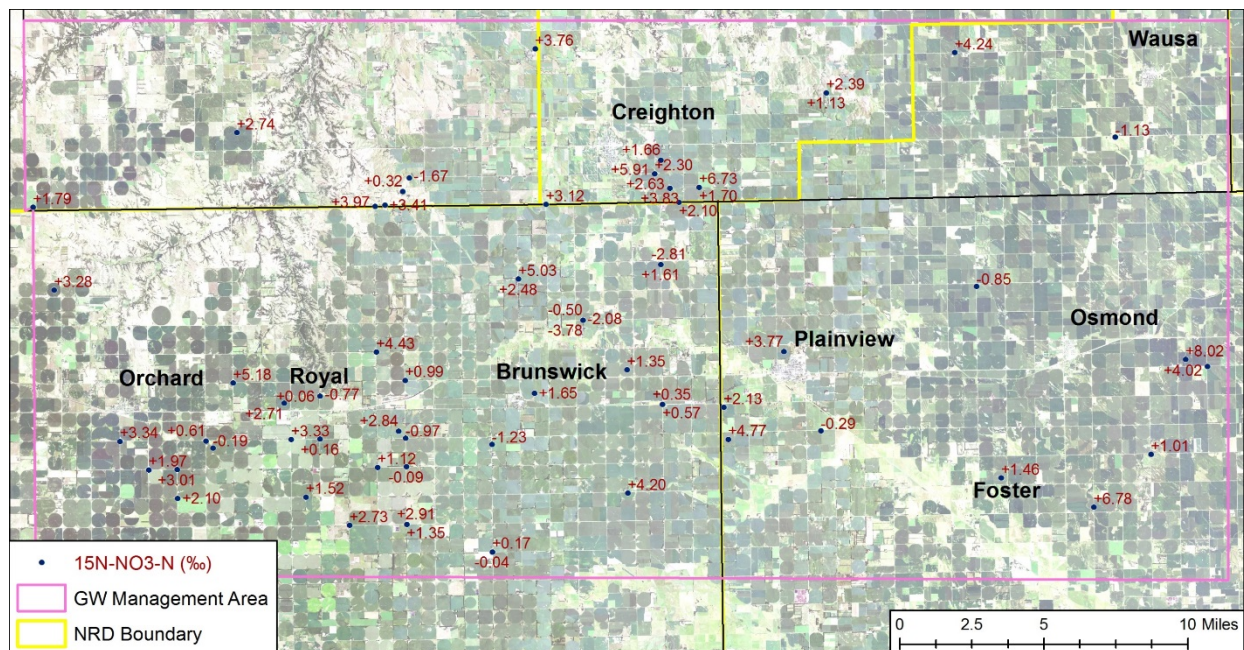
Figure 7. Spatial distribution of ^{15}N-NO$_3$ in samples from the Bazile Groundwater Management Area.

lower ^{15}N in contaminated groundwater at wastewater lagoons, but this situation would also result in enrichment of 18O-NO3 (Kendall et al 2008). Including both 15N and 18O analysis in this project helps evaluate whether or not organic sources of N are of particular concern at any of the locations. There is no supporting evidence from the N and O isotope analysis that livestock manure or wastewater is contributing substantial amounts of nitrogen to groundwater nitrate.

Dissolved Gases and Groundwater Age Dating

Because of transport times through the vadose zone, changing fertilizer application rates in individual areas will only be realized gradually. Dissolved gases and age dating can be used to delineate areas where recharge is more rapid, and potentially where changing nitrogen and irrigation water management can have the most rapid impact. Measuring stable isotopes of nitrate is one tool for tracing nitrate sources in groundwater and is quite different from "age-dating" ground water. Age-dating generally refers to the time that has elapsed since recharge water has reached the water table. This technique is possible because of predictable changes in atmospheric gases, such as chlorofluorocarbons, or through radioactive decay processes involving tritium (radioactive hydrogen). Elevated levels of tritium have occurred in the atmosphere and precipitation primarily from nuclear weapons testing in the 1950's and 60's (figure 8) though this high activity has decline considerably. Recharge water carries the tritium activity of precipitation. Tritium decays to a stable isotope of helium (^{3}He) at a constant rate (half-life = 12.3 years). As long as the proportion of tritium and ^{3}He can be accurately measured in a sample of groundwater, it can thus be used to age-date groundwater which has intercepted the water table within the last 40-50 years. Note that tritium activity in precipitation has stabilized since the 1970's so that the "bomb peak" recorded in the 1960's can no longer be used as a relative indicator of groundwater age.
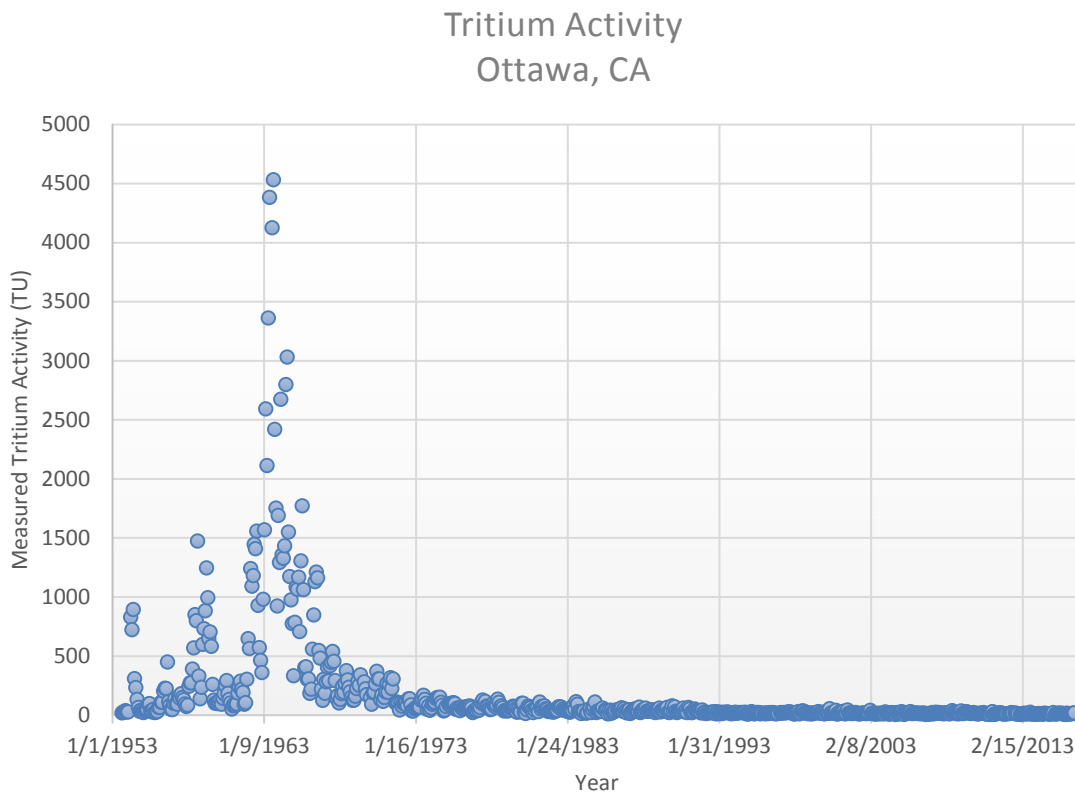
Figure 8. Variation in atmospheric tritium activity recorded in precipitation samples collected near Ottawa, Canada since 1953. Data from IAEA WISER – Water Isotope System for data analysis, visualization and Electronic Retrieval.

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Resampling for ground water age was conducted for in August 2017 for the ten wells across the area because samples collected in June 2016 were compromise by defective refrigeration clamps. The new samples for tritium helium age dating were collected and sealed in 3/8" copper tubes using custom fabricated tubing clamps in place of the commercial refrigeration clamps. Gas was extracted and measured using a custom-built high vacuum extraction system (Stanley, Baschek et al. 2009). Details of the extraction and analysis are reported in a later section. Because atmospheric sources of all gas species can affect the concentrations measured in groundwater samples, collection of sealed and intact samples is critical in providing useful results. Measure concentrations are summarized in Table 1.

Table 1. Results of dissolved gas analysis together with noble gas ratios, helium isotope enrichment (R/R$_{air}$), tritium activity measured using ^{3}He ingrowth. Apparent ages were estimated using an inverse modeling Excel workbook developed and described by Aeschbach-Hertig et al (1999; 2000) and requiring inputs of helium isotopes, tritium activities and noble gas concentration measurements.

Well ID	Sampling Date	NO$_3$N (mg/L)	N2 (cm³/gm)	Ar (cm³/gm)	Kr (cm³/gm)	Xe (cm³/gm)	Ne (cm³/gm)	^{4}He (cm³/gm)	^{3}He (cm³/gm)
201469/K-147	8/25/17	7.18	1.20E-02	3.38E-04	5.74E-08	5.52E-09	2.08E-07	1.69E-07	8.98E-14
201470/K-148	8/25/17	2.83	1.32E-02	3.52E-04	5.34E-08	4.70E-09	2.56E-07	7.35E-08	9.18E-14
137988/8S	8/24/17	9.64	1.36E-02	3.40E-04	5.33E-08	3.95E-09	2.51E-07	6.22E-08	1.53E-13
137989/9M	8/24/17	16.65	1.36E-02	3.82E-04	5.83E-08	4.34E-09	2.52E-07	4.86E-08	1.12E-13
137995/10M	8/24/17	14.72	1.48E-02	3.89E-04	6.18E-08	4.66E-09	2.76E-07	5.74E-08	1.51E-13
137998/11S	8/24/17	29.15	1.21E-02	3.43E-04	5.82E-08	3.80E-09	2.34E-07	4.49E-08	9.49E-14
138085/12S	8/24/17	27.80	1.17E-02	3.28E-04	5.61E-08	4.61E-09	2.30E-07	4.54E-08	9.29E-14
138103/14S	8/24/17	30.22	1.28E-02	3.47E-04	2.23E-08	1.45E-09	2.58E-07	4.84E-08	1.04E-13
G164448	8/25/17	0.01	Sample lost – Excess Helium					3.00E-07	
G164447	8/25/17	4.26	1.15E-02	3.36E-04	6.13E-08	1.461E-09	1.99E-07	4.03E-08	9.16E-14

Well ID	Sampling Date	^{22}Ne/^{20}Ne	^{129}Xe/^{132}Xe	^{86}Kr/^{84}Kr	R/R$_{air}$	^{3}H (TU)	Apparent Age (years)	Well Depth (ft)
201469/K-147	8/25/17	9.61E-02	9.99E-01	3.08E-01	0.28	BD	**	201
201470/K-148	8/25/17	9.60E-02	1.01E+00	3.07E-01	0.66	BD	**	201
137988/8S	8/24/17	9.29E-02	9.98E-01	3.04E-01	1.33	0.45	~ 50	67
137989/9M	8/24/17	9.69E-02	1.00E+00	3.08E-01	1.24	2.62	22.8	80
137995/10M	8/24/17	9.59E-02	1.00E+00	3.06E-01	1.41	1.67	39.4	140
137998/11S	8/24/17	9.47E-02	1.01E+00	3.06E-01	1.13	BD	**	90
138085/12S	8/24/17	9.56E-02	1.00E+00	3.06E-01	1.10	1.95	15.7	92
138103/14S	8/24/17	9.52E-02	1.00E+00	3.06E-01	1.15	1.43	24.8	69
G164448	8/25/17	NM	NM	NM	NM	BD	NM	230
G164447	8/25/17	9.98E-02	1.00E+00	3.08E-01	1.22	0.96	33.3	217

"NM" = Not measured, "BD" = Below Detection, "" = Could not be estimated**

Three samples (Wells "201469/K-147", "201470/K-148" and "G16448") contained high concentrations of helium with respect to air, likely from radiogenic or terrigenic helium sources in the aquifer - primarily naturally-occurring uranium and thorium. During extraction of G16448 the amount of helium recovered cause the instrument control software to abort the analysis, though the concentrations in the other two samples were below this threshold. These wells were among the deepest sampled and increased gas concentrations are consistent with sampling older groundwater increasing depth. Other dissolved gases show a composition similar to, or somewhat enriched compare to that of air in equilibrium with water.

Dissolved argon and nitrogen gas concentrations are slightly above that of air equilibrated water, and the ratio of dissolved argon to nitrogen is similar or slightly below the composition. Neon concentrations are higher than water in equilibrium with air, while xenon and krypton concentrations are both lower than that of water in contact with air. Tritium activities range between near our detection limit (0.1 TU) to a maximum of 2.62 TU and are consistent with activities expected from recent recharge from local precipitation (no anomalies). Groundwater with wells with excess helium could not be modeled or used for estimating time since recharge. Samples with measurable tritium activity were used to estimate the groundwater age, or elapsed time since the water had intercepted the water table. Overall the groundwater ages range between 15-50 years (Table 1). A map comparing the thickness of the unsaturated zone together with estimated groundwater ages is shown in figure 9. Deeper wells are in the upland areas and had excess helium from the aquifer. In theory, excess helium could be used to estimate residence time if the helium flux from the aquifer solids is known (Heaton 1984; Torgeson and Clarke 1985).

Overall, the distribution of dissolved gas concentrations, estimated ages, and nitrate isotope measurements all suggest that emphasis on controlling commercial nitrogen and irrigation water application rates should occur through the stream valleys of the Bazile Groundwater Management area. Valleys bounded by Creighton and Plainview, and on the west by Royal and Brunswick are generally shallower, recharge likely to be more rapid, and thus more highly susceptible to nitrate leaching. The ages also indicate that any response to reduced nitrate leaching will likely require a minimum of 15-30 years to be observed at the depths sampled by these wells.
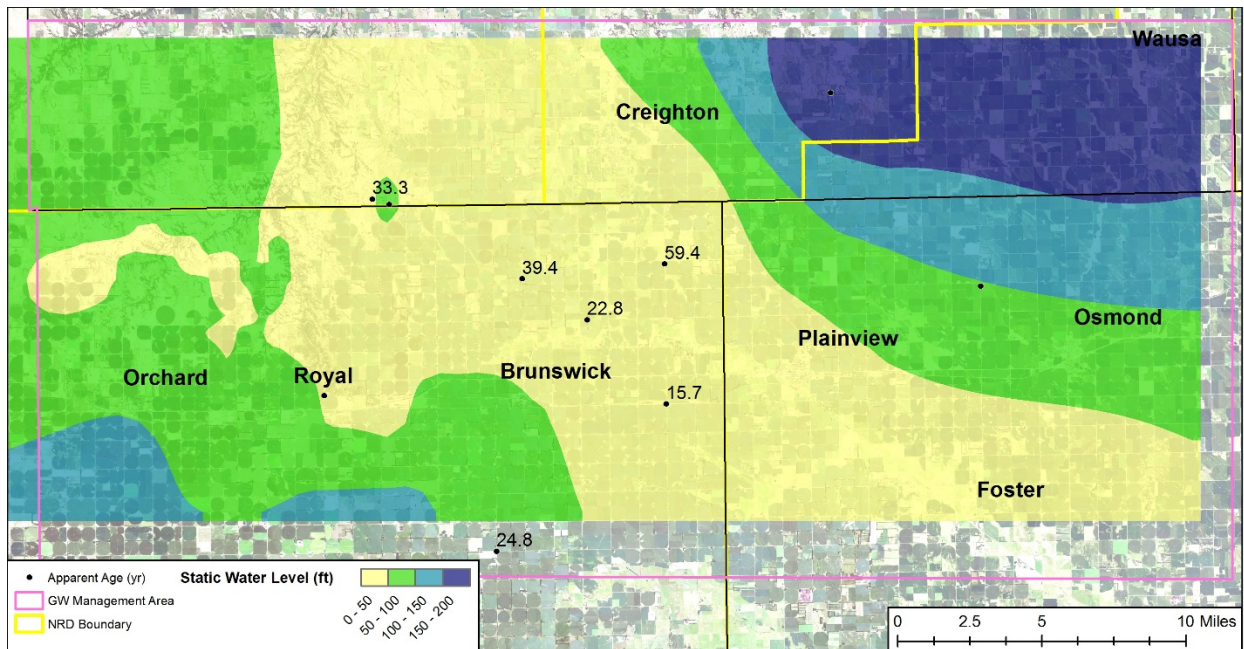
Figure 9. Distribution of groundwater ages estimated using the helium-tritium and noble gas measurements from selected monitoring wells compared to the interpolated vadose zone thickness across the Bazile Groundwater Management Area. Resolution of vadose zone thickness controlled only using sampled monitoring wells.

Field Parameters and Water Chemistry

Sampling of the monitoring wells for noble gas analysis occurred in 2016 and 2017, though the 2016 samples were compromised by the defective refrigeration clamps. In 2017, all wells sampled for noble gas measurements included measurements of depth to water, field parameters using a portable Hydrolab, and samples for other dissolved gases and anions (Table 2). This data was collected the intention of gaining additional information to be used in evaluation of the age dating results, and potential for nitrate

attenuation in the aquifer. A comparison of the ages with groundwater silica, measured on samples collected in 2016, suggests that silica may not be a useful predict of groundwater residence time. A plot of dissolved nitrate-N concentrations versus nitrous oxide (N_2O) concentrations (figure 10) suggests that nitrous oxide is directly related to nitrate-N concentrations, consistent with nitrous oxide produced via nitrification. Elevated nitrous oxide concentrations can be found in ground water where denitrification is actively removing nitrate-N. A study of shallow groundwater denitrification in the Central Platte NRD (Spalding and Parrott, 1994) measured groundwater nitrous oxide concentrations up to 7 µmol/L, or roughly 10 times higher than the highest concentration measured in these wells. While there may be other locations in the Bazile Groundwater Management Area where denitrification is occurring, nitrate in these wells has likely not been affected by this attenuation process. The absence of nitrite-N, an important intermediate during denitrification of nitrate to nitrogen gas, together with moderate to high concentrations of dissolved oxygen in these wells also suggests that denitrification may not be active in groundwater collected from these wells (Table 2).

Table 2. Summary of field measurements (water table "WT" depth, Electrical Conductivity (EC), dissolved oxygen (D.O.)), compared with dissolved gas concentrations and anion analysis, compared with silica measurements made in samples collected in 2016.

		2016	Field Measurements			Dissolved Gases (umoles/ L)			Anions (mg/L)					
Well ID	Alt ID	Silica (mg/L)	WT Depth (ft)	EC (uS/cm)	D.O. (mg/L)	CO_2	CH_4	N_2O	Fluoride	Chloride	Nitrite-N	Bromide	Nitrate-N	Sulfate
137988	8S	67.0	5.35	522.1	3.4	3634	0.23	0.40	0.22	3.19	ND	ND	9.1	14.6
138103	14S	56.3	45.1	642.0	11.0	2892	0.23	0.62	0.33	8.81	ND	ND	25.1	17.3
G-164447	LNNRD	76.1	67.2	322.0	10.9	2355	0.18	0.35	0.18	2.89	ND	ND	4.8	10.6
137998	11S	56.2	67.4	544.0	10.5	3070	0.18	0.63	ND	6.41	ND	ND	24.0	22.4
138085	12S	57.7	69.1	513.0	10.4	2541	0.24	0.61	ND	5.37	ND	ND	23.2	19.3
G-164448	LNNRD	71.3	88.4	163.3	10.2	1613	0.23	0.32	0.38	0.20	ND	ND	0.3	2.9
137995	10m	54.1	95.9	265.0	11.9	1474	0.20	0.35	ND	1.63	ND	ND	12.0	13.1
138129	15S	55.7	100.1	414.7	10.8	1821	0.21	0.47	ND	4.25	ND	ND	18.6	9.7
GI54414	K-148	NM	187.2	648.0	6.2	4213	0.38	0.39	ND	3.57	ND	ND	2.2	73.5
GI54413	K-147	NM	200	602.0	5.7	3941	0.75	0.26	0.23	3.92	ND	ND	7.3	40.6

Knowledge Gained and Recommendations

Knowledge gained from nitrate isotope analysis can give insight into the major nitrogen sources and transformation chemistry of nitrogen in the groundwater. Having this knowledge provides a solid foundation for the NRDs to share with residents the relationships between actions taken on the surface with what occurs in the groundwater. Information gained from this study will also give credence to present and future management actions by the NRDs.

This project should help provide the NRDs and other agencies with talking points for communications to support actions taken to manage nitrogen fertilizer applications. It may also provide communities with information needed for creation of wellhead protection plans. This study re-sampled locations tested in 2001 for ^{15}N-NO_3 as well as sub-sampled locations for ^{18}O-NO_3 to provide insight into how much nitrogen present is due to denitrification, volatilization or mixing of distinct sources. No previous ^{18}O-NO_3 analysis had been done in the Bazile GWMA, and the addition of
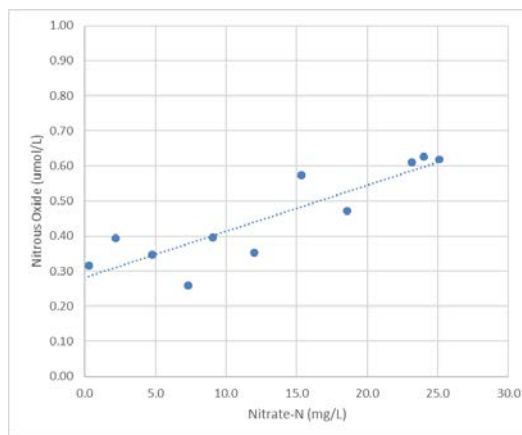
Figure 10. Relationship between nitrate-N and nitrous oxide concentrations in samples from the monitoring wells sampled for age dating.

this analysis provided the researchers increased confidence when interpreting collected ^{15}N data. Dedicated monitoring wells sampled along with irrigation wells for each township with the highest nitrate concentrations all suggest that leaching of commercial fertilizer is the primary source for nitrate. Groundwater ages indicate that it will require at least 15-30 years after a significant reduction in nitrate loading from the vadose zone will be reflected in ground water nitrate for this area. Data collected during this project helps identify major sources of nitrogen in the newly added areas of the Bazile GWMA as well as creating baseline data for future studies. Vadose zone monitoring in well head protection areas, as well as those locations with a greater depth to water may, identify areas were stored nitrate has accumulated above the water table and help predict when to expect loading to occur.

Measurement of Stable Isotopes in Nitrate
Samples for nitrogen isotope analysis were prepared according to methods previously described (Kreitler 1975, Gormly and Spalding 1979) and the same as used previously in the Creighton area (Burbach and Spalding 2001). Briefly, nitrate reduced to ammonia with Devardas alloy, distilled into a boric acid indicator solution, and determined titrimetrically with standardized sulfuric acid. Distillates were acidified with 1N sulfuric acid immediately after titration and evaporated to 1 to 2 mL on a hot plate, and then reacted with lithium hypobromite on a high-vacuum preparation line and the ammonium quantitatively reduced to nitrogen gas, purified by passage through two liquid nitrogen cryotraps and a 400oC copper oven, and collected in a gas sample bulb. Atmospheric nitrogen standards are prepared on the same high-vacuum preparation line. Ultrapure tank nitrogen is used as the working standard and is calibrated against the atmospheric nitrogen standard. All nitrogen isotope measurements were performed on either a VG Instruments OPTIMA or a GVI Isoprime dual inlet stable isotope ratio mass spectrometer (IRMS). The OPTIMA was purchased in 1992 as a state-of-the-art IRMS with improved ion optics, amplifier design, and electronics which improved both the sensitivity and precision of nitrogen isotope ratio measurements. It has an absolute sensitivity of 1500 molecules of CO_2 per mass 44 ion, and has been fitted with a nitrogen "cold finger" cryo-trap which reduces the sample size requirements for nitrogen to 20 bar µL, equivalent to ~23 µg N, or about 0.2 mg/L NO3-N. The internal precision of the OPTIMA is 0.01 ‰. The GVI Isoprime was purchased in 2007 with specifications that match or exceed the OPTIMA. The δ15N of the sample was measured and expressed relative to the atmospheric standard expressed in parts per thousand (‰). Quality control was monitored through the analysis of replicate standards to determine the accuracy and repeatability of the method. The sample standard deviation for 20 identical preparations of an ammonium standard of known isotopic composition was ±0.5‰. The standard deviation of a similar number of nitrate-N working standards was ±0.6‰. The standard deviation for 216 preparations of the working gas standard was ±0.05‰. The relative percent difference from the analysis of 39 sets of duplicate samples was 0.59‰.

Samples for determination of oxygen isotope composition of nitrate were prepared according to methods described in Chang et al 1999 and Silva et al 2000. Nitrate concentration is first determined using the Cd-reduction method (Std. Methods 4500-NO_3F) to determine required sample volume. Then, a measured volume of sample containing 0.25 mg NO3-N is treated with 1M barium chloride to precipitate sulfate and phosphate. The solution is then filtered, and then passed through a cation exchange column to remove excess Ba^{2+}, and then through an anion exchange column to concentrate nitrate. Nitrate is eluted using 3 M hydrochloric acid, neutralized with Ag_2O, filtered to remove the AgCl precipitate, and then dried to producing purified $AgNO_3$. The $AgNO_3$ is then dissolved in 1ml of reagent water and 100 µL (25 µgN) aliquots transferred to three silver cups and dried for analysis of oxygen isotope composition using high temperature pyrolysis on nickelized graphite in a closed tube to produce carbon monoxide (CO) on a Eurovector EA Isoprime continuous flow isotope ratio mass spectrometer. The final result is averaged from the triplicate instrumental results and converted to the standard oxygen isotope reference (VSMOW =0.00 ‰). A reagent grade potassium nitrate (KNO3) is used as a working standard, and reference sucrose oxygen isotope standard (obtained from Elemental Microanalysis) are analyzed with every sample batch (up to 20 samples) both to calibration and for drift correction. USGS 34 and USGS 35

reference standards are analyzed at least monthly to compare and convert working standards to a $\delta18O$ isotope value with respect to VSMOW. The 1σ measured analytical precision of $\delta^{18}O$-NO3 is ±0.5‰ for solutions of KNO3 standard processed through the entire procedure. In addition to triplicate instrumental average measurement, laboratory duplicates were carried through the preparation process and analyzed at a rate of 5%.

Measurement of Dissolved Noble Gases, Tritium, Anions, and Silica
Extraction and analysis of noble gases and helium isotopes has been used for groundwater age dating since the early 1990's and methods for quantification have evolved to take advantage of changes in technology. The apparatus and equipment used to process samples is not available commercially and must be assembled on-site. Samples collected for this project were collected in sealed 3/8" O.D. copper tubes and sealed using clamps fabricated and specifically designed for this purpose. Each sample tube is mounted on an 8-port, custom-built high vacuum manifold using 3/8" Swagelok connections above a 200 milliliter a stainless steel receiving vessel. After evacuation and ensuring that the connections are leak tight, a system blank is run for each port overnight. The next day each sample is sequentially de-crimped and opened to the receiving vessel for extraction of sample gases under vacuum. Water and carbon dioxide are removed as gases pass first through ethanol slurry and liquid nitrogen traps, and subsequently into a ultra-low temperature cyrogenic water trap maintained at $180^{o}K$. Nitrogen, argon, oxygen, krypton and xenon are trapped on a vacuum insulated, bare stainless steel trap maintained at $24^{o}K$ by a CTI Cryogenics refrigeration and cold head unit. Helium and neon are trapped on a second carbon-coated trap cooled to $10^{o}K$. After trapping is complete, each gas is sequentially released and measured by slowly heating the trap into a selected detector. Oxygen is scrubbed from the sample gas using a heated SAES titanium getter to allow quantitative measurement of argon. Concentrations of nitrogen and argon are measured on capacitance manometers, while neon, krypton and xenon are measured on a Hiden Instruments quadrupole mass spectrometer. Helium-4 and helium-3 are measured separately on a Thermo Helix SFT high resolution noble gas mass spectrometer. All detectors are calibrated using standardized atmosphere with individual gases separated, purified and measured under the same conditions as samples.

After the water sample has been degassed, it is resealed in the stainless-steel flask for tritium measurement using helium-3 ingrowth. The ingrowth period requires a minimum of 4-6 weeks, though a longer period (up to 4-6 months) can be required when tritium activity is low. Helium-3 is measured using the Thermo Helix SFT mass spectrometer calibrated with an ultra-low level air standard and corrected for background. Groundwater ages were estimated using tritium-helium age-dating with appropriate corrections for estimated recharge temperature (Solomon and Sudicky 1991, Cey, Hudson et al. 2009). The models use the measured dissolved gas concentrations and helium isotope ratios to determine recharge temperature, pressure, salinity, excess air, and the degree to which the gases have been fractionated, due to differences in gas solubilities. Calculations use an inverse modeling approach where each the variables listed above are varied in order to produce a least Chi-squared test, which is a sum of the error-weighted deviations between modelled and measured gas concentrations. Ground water ages are based on the Closed System Equilibration (CE) model developed by Aeschbach-Hertig et al. (2000). Assumptions include that barometric pressure is determined by recharge elevation and salinity is negligible for fresh groundwater. Recharge temperatures are based on known solubilities and expected isotope fractionation. Nitrous oxide and methane concentrations were measured on separate ground water samples collected in helium-flushed glass serum vials during August 2018. Prior to gas analysis, samples equilibrated in a 20 °C water bath. Headspace analysis was completed by gas chromatography (model SRI 8610C) at the University of Nebraska USDA Agricultural Research Service Laboratory. Anions were measured following Standard Methods SM4110 on a Dionex ICS-90 ion chromatograph (APHA, 2014) using an AS14 ion exchange column. Dissolved silica was measured colorimetrically as molybdate-reactive silica on a Seal AQ2 autoanalyzer SM4500SiO2-C (APHA, 2014).

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Summary Table of Nitrate Concentrations and Isotope Results

"NM" Indicates not measured.

WSL Lab ID#	Sample ID	Collection Date	NO$_3$-N (mg/L)	^{15}N-NO$_3$ (‰)	NH$_4$-N (mg/L)	^{15}N- NH$_3$ (‰)	Batch	Analysis Date
15-2542	NW 20-29-7W	8/3/2015	13.7	2.7	0.1	NM	W15283	1/15/2016
15-2543	SE 1-29-6W	8/3/2015	22.5	3.8	0.0	NM	W15283	1/15/2016
15-2544	SW 31-29-8W	8/3/2015	8.8	1.8	0.1	NM	W15283	1/15/2016
15-2545	SW 25-27-7W	8/3/2015	10.3	2.7	0.0	NM	W15283	1/15/2016
15-2546	NW 27-27-7W	8/3/2015	26.1	1.5	0.1	NM	W15283	1/15/2016
15-2547	SW 32-28-7	8/3/2015	12.7	5.2	0.1	NM	W15283	1/19/2016
15-2548	SW 10-27-8W	8/3/2015	22.6	3.3	0.1	NM	W15283	1/19/2016
15-2549	SE 14-27-8W	8/12/2015	29.0	3.0	0.2	NM	W15283	1/19/2016
15-2550	SW 24-27-8W	8/12/2015	14.5	2.1	0.2	NM	W15283	1/19/2016
15-2551	SE 12-27-8W	8/12/2015	19.7	0.6	0.1	NM	W15283	1/19/2016
15-2552	NW18-27-7W	8/12/2015	33.3	-0.2	0.1	NM	W15283	1/19/2016
15-2553	SE 18-28-8W	8/12/2015	8.6	3.3	0.1	NM	W15283	1/19/2016
15-2554	NE16-27-7W	8/12/2015	16.9	3.3	0.1	NM	W15283	1/20/2016
15-2555	SW 11-27-7W	8/12/2015	26.4	0.2	0.0	NM	W15283	1/20/2016
15-2556	NE 25-28-7W	8/13/2015	10.5	4.0	0.1	NM	W15283	1/20/2016
15-2557	NW 31-28-6W	8/13/2015	26.5	4.4	0.1	NM	W15283	1/20/2016
15-2558	NE 29-28-6W	8/13/2015	11.9	3.1	0.1	NM	W15283	1/20/2016
15-2559	SE 7-27-6W	8/13/2015	26.3	2.8	0.0	NM	W15283	1/20/2016
15-2560	NW 20-27-6W	8/13/2015	24.9	-0.1	0.1	NM	W15283	2/5/2016
15-2561	NE 32-27-6W	8/13/2015	20.4	2.9	0.1	NM	W15283	2/5/2016
15-2566	BB-NRD-15-154	8/24/2015	5.6	6.8	0.1	NM	W15285	7/28/2016
15-2567	BB-NRD-15-155	8/24/2015	25.8	1.5	0.1	NM	W15285	7/28/2016
15-2568	BB-NRD-15-156	8/24/2015	21.1	2.1	0.1	NM	W15285	7/28/2016
15-2569	BB-NRD-15-165	8/24/2015	0.8	NM	0.3	NM	W15285	

WSL Lab ID#	Sample ID	Collection Date	NO$_3$-N (mg/L)	^{15}N-NO$_3$ (‰)	NH$_4$-N (mg/L)	^{15}N- NH$_3$ (‰)	Batch	Analysis Date
15-2570	BB-NRD-15-172	8/24/2015	21.1	3.8	0.2	NM	W15285	7/28/2016
15-2571	BB-NRD-15-173	8/24/2015	23.8	4.8	0.2	NM	W15285	7/28/2016
15-2572	BB-NRD-15-179	8/24/2015	14.9	8.0	0.2	NM	W15285	7/28/2016
15-2573	BB-NRD-15-199	8/24/2015	2.4	4.2	0.1	NM	W15285	7/28/2016
15-2574	O7S-15	9/16/2015	12.7	-0.3	0.1	NM	W15285	7/28/2016
15-2575	O8M-15	9/17/2015	13.3	1.0	0.1	NM	W15285	7/28/2016
15-2576	20M-15	9/17/2015	0.5		0.1	NM	W15285	
15-2577	O3S-15	9/17/2015	14.1	-1.2	0.1	NM	W15285	7/28/2016
15-2578	19S-15	9/17/2015	1.0	-1.1	0.1	NM	W15285	7/28/2016
15-2579	O2M-15	9/21/2015	14.2	4.0	0.1	NM	W15285	7/28/2016
15-2580	K3981415	8/14/2015	27.0	2.1	0.1	NM	W15285	7/28/2016
15-2581	K-145-9-9-15	9/9/2015	20.5	1.7	0.1	NM	W15285	7/28/2016
15-2586	SE 4-27-7W	8/13/2015	13.1	2.7	0.1	NM	W15287	9/28/2016
15-2587	NE 22-27-8W	8/25/2015	23.3	2.0	0.1	NM	W15287	9/28/2016
15-2588	NE 24-27-7W	8/25/2015	19.1	1.1	0.1	NM	W15287	9/28/2016
15-2589	SE 30-27-6W	8/25/2015	18.7	1.3	0.1	NM	W15287	9/28/2016
15-2590	NW 17-27-6W	8/25/2015	21.2	-1.0	0.1	NM	W15287	9/28/2016
15-2591	NE 6-27-6W	8/25/2015	18.9	1.0	0.1	NM	W15287	9/28/2016
15-2592	NE 28-27-5W	8/25/2015	27.6	4.2	0.1	NM	W15287	9/28/2016
15-2593	SE 33-28-5W	8/25/2015	23.4	1.3	0.2	NM	W15287	9/28/2016
15-2594	SW 1-27-6W	8/27/2015	19.0	1.7	0.2	NM	W15287	9/28/2016
16-1558	MW-2D-12-14-15	12/14/2015	17.2	1.7	0.1	NM	W16121	4/20/2017
16-1559	MW-4M-12-14-15	12/14/2015	6.6	2.3	0.0	NM	W16121	4/20/2017
16-1560	MW-3M-12-14-15	12/14/2015	13.1	2.6	0.0	NM	W16121	4/20/2017
16-1561	K-148-12-8-15	12/8/2015	1.8	1.1	0.0	NM	W16121	4/20/2017
16-1562	K-147-12-8-15	12/8/2015	5.8	2.4	0.1	NM	W16121	4/20/2017
16-1563	MW3-3D-12-14-15	12/14/2015	10.9	3.8	0.1	NM	W16121	4/20/2017
16-1564	MW3-4D-12-14-15	12/14/2015	14.7	5.9	0.1	NM	W16121	4/20/2017

WSL Lab ID#	Sample ID	Collection Date	NO$_3$-N (mg/L)	^{15}N-NO$_3$ (‰)	NH$_4$-N (mg/L)	^{15}N- NH$_3$ (‰)	Batch	Analysis Date
16-1565	MW3-2M-12-14-15	12/14/2015	12.2	6.7	0.0	NM	W16121	4/20/2017
16-1566	SW 20-28-5W	10/9/2015	5.7	-3.8	0.0	NM	W16121	4/20/2017
16-1567	SE 34-27-6W	10/9/2015	12.3	0.2	0.0	NM	W16121	4/20/2017
16-1568	NE 15-28-5W	10/9/2015	6.1	-2.8	0.0	NM	W16121	4/20/2017
16-1569	SW 13-28-6W	10/9/2015	12.8	5.0	0.0	NM	W16121	4/20/2017
16-1570	SE 3-27-5W	10/9/2015	25.1	0.4	0.0	NM	W16121	4/20/2017
16-1571	SW 2-27-7W	10/9/2015	24.2	-0.8	0.0	NM	W16121	4/20/2017
16-1572	15-S	10/9/2015	17.3	-0.9	0.0	NM	W16121	4/20/2017
16-2342	WEST KNOW RW #1	6/17/2016	2.0	-1.7	0.0	NM	W16216	4/20/2017
16-2344	SOUTHWELLLNNWN	6/17/2016	2.3	-2.1	0.0	NM	W16216	4/20/2017
17-4514	201469/K-147	8/25/2017	6.9	5.3	0.0	NM	W17781	12/8/2017
17-4516	201470/K-148	8/25/2017	2.2	3.4	0.0	NM	W17781	12/8/2017
17-4517	138129/15S	8/24/2017	18.3	0.3	0.0	NM	W17781	12/8/2017
17-4518	137988/8S	8/24/2017	8.7	1.6	0.0	NM	W17781	12/8/2017
17-4519	137989/9M	8/24/2017	16.0	-0.5	0.0	NM	W17781	12/8/2017
17-4520	137995/10M	8/24/2017	13.7	2.5	0.0	NM	W17781	12/8/2017
17-4521	137998/11S	8/24/2017	26.1	0.1	0.0	NM	W17781	12/8/2017
17-4522	138085/12S	8/24/2017	27.4	0.6	0.0	NM	W17781	12/8/2017
17-4523	138103/14S	8/24/2017	24.5	0.0	0.0	NM	W17781	12/8/2017
17-4524	G164448	8/25/2017	1.4	0.9	0.0	NM	W17781	12/8/2017
17-4525	G164447	8/25/2017	6.0	-0.6	0.0	NM	W17781	12/8/2017
17-4526	138085/12S REP	8/24/2017	25.1	0.7	0.0	NM	W17781	12/8/2017