Iowa DNR Ambient Groundwater Quality Monitoring Program Summary for FY19

Introduction: The purpose of the Iowa Department of Natural Resources' (IDNR's) ambient groundwater monitoring program is to document the quality of water in Iowa's aquifers, which are the major sources of drinking-water in Iowa. Results from this program help us to understand which constituents are present and how their concentrations vary spatially and over time, and to better understand the relationships between water quality, geology, well construction, pumping rates, and land-use practices.

This report summarizes the results of the fiscal year 2019 (FY19) groundwater monitoring effort. Ambient groundwater quality monitoring in FY19 was focused on three objectives.

1) To evaluate spatial and temporal variations in water quality by monitoring of untreated groundwater from public water supply wells with an emphasis on wells susceptible to surface contamination.
2) To use isotopic ratios of nitrogen and oxygen to better understand sources of nitrate in groundwater.
3) To establish baseline water quality for six unpumped monitoring wells in the Silurian-Devonian aquifer constructed by the Iowa Geological Survey and historically used for water level monitoring.

1. Water quality monitoring of municipal wells

Untreated groundwater samples were collected from 79 public water supply wells (Figure 1). These wells represented all major aquifer systems and a wide range of depths, but the primary focus of this sampling was on wells susceptible to anthropogenic contamination based on estimated confining layer thicknesses (Table 1). Samples were collected between December 2018 and April 2019 by certified water operators. IDNR staff collected duplicate samples at ten of the monitoring locations for quality control, along with two field blanks. Samples were submitted to the State Hygienic Laboratory (SHL) for analysis of pH, specific conductivity, total dissolved solids, total alkalinity, nitrate + nitrite as nitrogen (N), ammonia as N, orthophosphate as phosphorus (P), chloride, sulfate, iron, manganese, magnesium, potassium, calcium, and sodium. Results are summarized in Table 2. Results from FY19 for two constituents of concern, manganese and nitrate, were analyzed in detail and evaluated with respect to historical records.

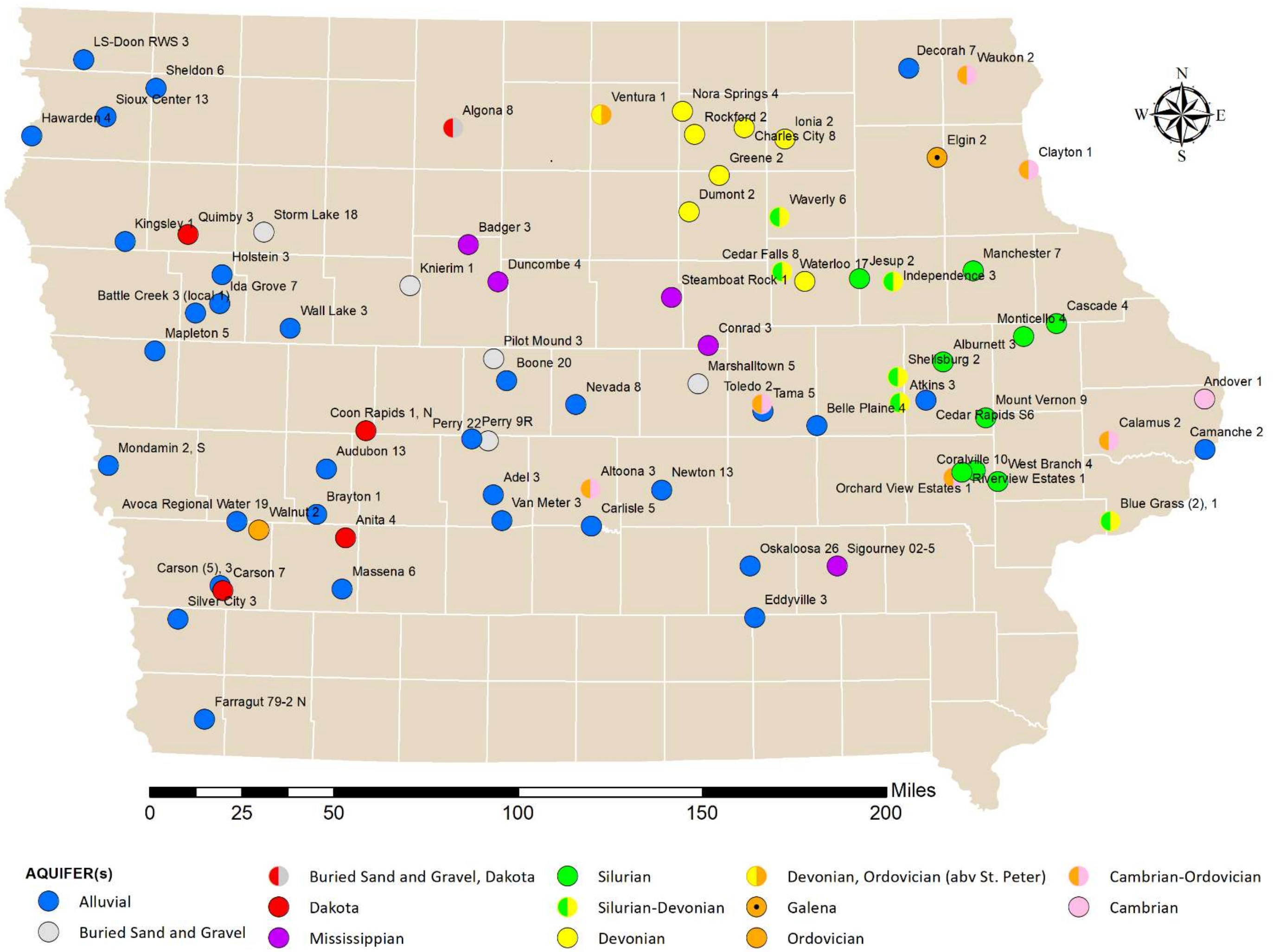


Figure 1. Groundwater quality monitoring locations for FY19 by aquifer.

Table 1. Summary of well characteristics for FY19.

Aquifer System	Number	Percentage	Age (Date Drilled)	Number	Percentage
Alluvium (Holocene)	32	41%	1899 - 1970	21	27%
Buried Sand and Gravel (Pleistocene)	5	6%	1970 - 1988	33	42%
Dakota (Cretaceous)	4	5%	1990 - 2010	25	32%
Mississippian	5	6%			
Silurian-Devonian	23	29%	**Well Status**	**Number**	**Percentage**
Cambrian-Ordovician	9	11%	Active	72	91%
Multiple Aquifer systems	1	1%	Standby	6	8%
			Not Used	1	1%
Vulnerability	**Number**	**Percentage**	**Well Depth**	**Number**	**Percentage**
High (<50 ft confining layer thickness)	51	65%	20 - 100 ft	35	44%
Intermediate (50 - 99 ft confining thickness)	11	14%	115 - 500 ft	33	42%
Low (≥100 ft confining thickness)	17	22%	548 - 2635 ft	11	14%

Table 2. Summary of water quality results for untreated groundwater samples collected from 79 public water supply wells in Fiscal Year 2019. All analyses performed by the State Hygienic Laboratory. For median and 75th percentile, values below the quantitation limit were assigned values of half the quantitation limit.

Analyte	Method	Quantitation limit	Det. Freq.	Mean of Detects	Median	75th Percent -ile	Max
Laboratory pH	SM 4500 H+B	--	100%	7.5	7.5	7.6	11
Total Dissolved Solids	SM 2540 C	1.0	100%	494	450	560	1640
Specific Conductance	SM 2510 B	1 umho/cm	100%	796	750	890	2300
Total Alkalinity	SM 2320 B	1 mg/L	100%	288	280	340	480
Chloride (Cl)	EPA 300.0	0.5 – 50 mg/L	96%	28	16	33	230
Sulfate (SO_4)	EPA 300.0	1 – 100 mg/L	100%	81	47	80	720
Iron (Fe)	EPA 200.7	0.02 mg/L	32%	0.78	0.01	0.05	7
Manganese (Mn)	EPA 200.7	0.02 mg/L	48%	0.35	0.01	0.16	1.4
Magnesium (Mg)	EPA 200.7	0.5 mg/L	99%	33.0	32.0	39.0	68
Calcium (Ca)	EPA 200.7	1 mg/L	100%	99	100	120	190
Potassium (K)	EPA 200.7	1 mg/L	97%	4.0	2.7	3.7	39
Sodium (Na)	EPA 200.7	0.5 mg/L	100%	30	16	29	220
Ammonia-nitrogen as N	LAC 10-107-06-1J	0.05 mg/L	53%	0.82	0.08	0.54	5.2
Nitrate + Nitrite as N	LAC 10-107-04-1J	0.1 - 0.5 mg/L	52%	5.03	0.14	3.5	33
Orthophosphate as P	LAC 10-115-01-1A	0.02 mg/L	35%	0.12	0.01	0.03	0.91

Manganese

Manganese is a naturally-occurring element in groundwater. In 1979, the US EPA established a secondary drinking-water standard of 0.05 mg/L in order to avoid taste, odor, and staining caused by manganese. In 2004, the US EPA published three health advisories for manganese in drinking water:

- Acute, short-term health advisory (HA) for bottle-fed infants up to 6 months of age, who should not be given water with manganese concentrations greater than 0.3 mg/L for more than a total of 10 days per year. This includes formula made with the tap water.
- Acute, short-term HAL for the general population, who should not ingest water with manganese concentrations greater than 1 mg/L for more than a total of 10 days per year.
- Chronic, lifetime HAL for manganese in drinking water of 0.3 mg/L which is intended to be protective of life-time exposure for the general population.

Neither the secondary drinking water standard or the health advisories are enforceable drinking water standards, but Iowa requires public notice for systems that exceed the short-term HA in finished water. They are provided as guidance to drinking water providers. Additional information regarding the health advisories for manganese can be found here: https://www.iowadnr.gov/Environmental-Protection/Water-Quality/Drinking-Water-Compliance/Drinking-Water-Health-Advisories

Thirty-one (39%) of the wells sampled in FY19 contained levels of manganese above the secondary drinking water standard of 0.05 mg/L. As has been observed in the past, elevated manganese concentrations occurred more frequently in the western and southern portions of the state (Figure 2). None of the wells tested in NE Iowa's Field Office #1 region in FY19 contained levels of manganese over the secondary drinking water standard of 0.05 mg/L; however, wells drawing water from alluvial deposits adjacent to the Mississippi River have had detections of manganese in the past.

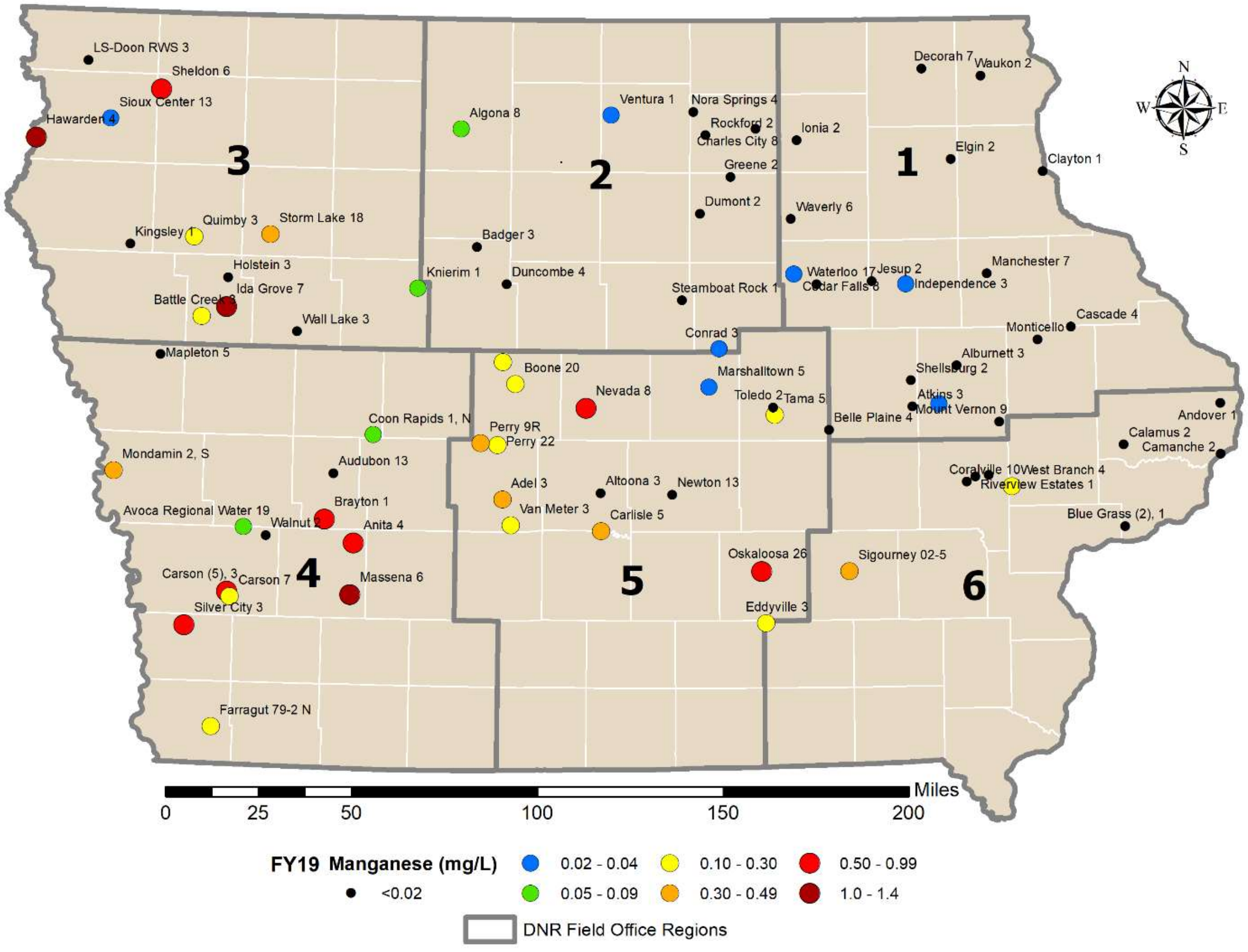


Figure 2. Concentrations of manganese in raw water from municipal wells sampled in FY19.

As in previous summaries of Iowa's groundwater quality, the highest manganese concentrations were found in alluvial wells (Figure 3), which was also the aquifer system sampled most frequently. Concentrations above the secondary drinking-water standard were found in all major aquifer systems, with the exception of the Cambrian-Ordovician system. Concentrations of manganese above EPA's lifetime health advisory level (0.3 mg/L = 300 µg/L = 300 ppb) were found in all aquifer systems in FY19, with the exception of the Silurian-Devonian and Cambrian-Ordovician systems (Figure 3).

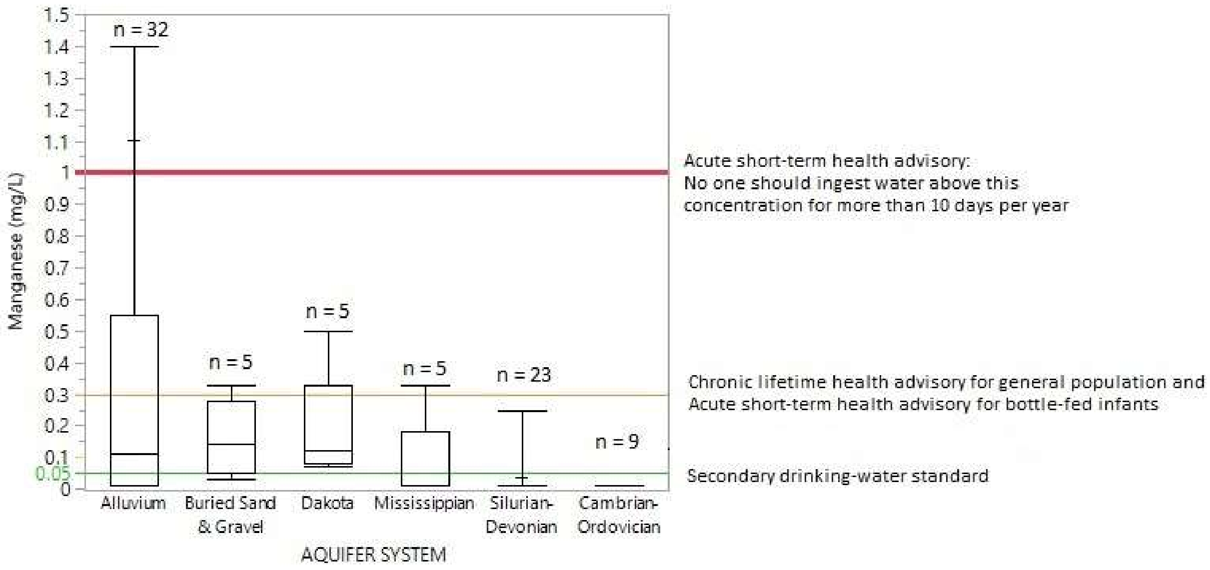


Figure 3. Quartile boxplots show distributions of manganese concentrations by aquifer system for public water supply wells sampled in FY19 relative to health advisory levels. It should be noted that these are from untreated samples, not finished drinking-water.

Since 2002, the ambient groundwater quality monitoring program has obtained 671 results of manganese analyses from 416 public water supply wells. Of those samples, 291 (43%) contained no detectable manganese above the quantitation limit of 0.02 mg/L, and 351 (52%) had concentrations of manganese below the secondary drinking water standard of 0.05 mg/L. 140 samples representing 91 public water supply wells (in 77 communities) had reported concentrations above the health advisory level of 0.3 mg/L. These wells were most often located in alluvial aquifers (65%), but some were also from Buried Sand & Gravel (11%), Dakota (16%), Mississippian (3%), and Silurian (1%) aquifers. These results are consistent with assessment of manganese in principle aquifers of the Unites States (McMahon and Chapelle, 2008). Of the wells that were sampled more than once between 2002 and 2019, those that tested negative for manganese generally remained below detection, while some of the wells that tested positive for manganese had concentrations varying as much as 1 mg/L.

Reduction/oxidation (redox) conditions influence the chemistry, mobility, and concentrations of certain water constituents in groundwater (Eberts et al., 2013; McMahon and Chappelle, 2008). For example, oxic conditions (dissolved oxygen >0.5 mg/L) favor the oxidation of manganese into solid manganese oxides (not mobile in groundwater) and the transformation of ammonia to highly mobile nitrate (nitrification). Low oxygen (anoxic) environments favor the microbially mediated reduction of nitrate to nitrite to nitrous oxide (denitrification), followed by reduction of manganese from oxide minerals to the dissolved (mobile) form. Redox conditions can vary with depth, organic carbon content, and water age. Municipal wells often draw water from a range of depths and mixing from multiple water-bearing units may occur. Figure 4 shows the concentrations of manganese and nitrate concentrations in FY19 samples. When both nitrate and dissolved manganese occur in the same sample, this is an indication that groundwater sources are mixing in the well.

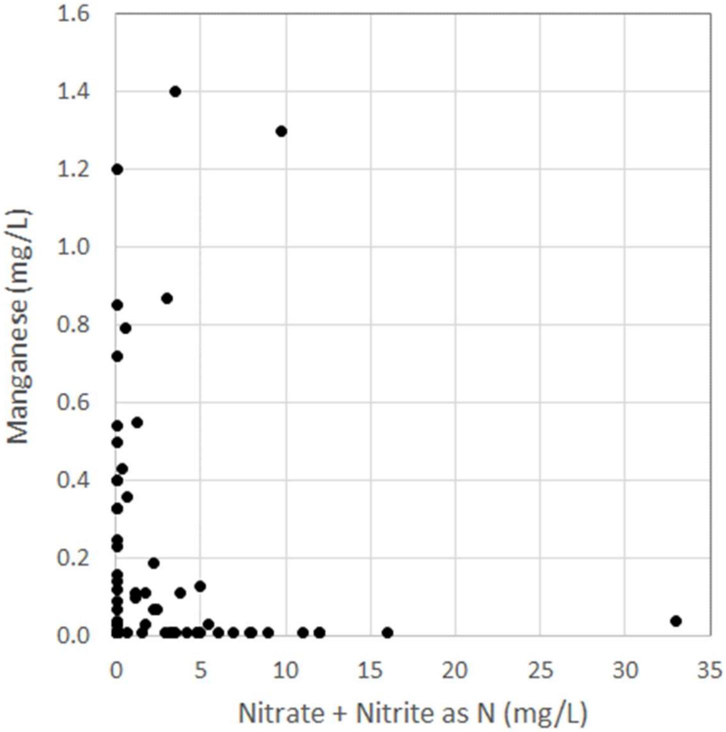


Figure 4. Nitrate + Nitrite as N vs. manganese concentrations in FY19 samples.

Nitrate occurrence

Nitrate continues to be a challenge for some public drinking water systems that are required to meet the US EPA's primary drinking water standard of 10 mg/L as nitrogen (N), which is based on an association between nitrate and methemoglobinemia (blue-baby syndrome) in infants. Recent studies suggest an association between increased risk for some types of cancer, thyroid disease, and neural tube defects associated with ingestion of nitrate in drinking water, at concentrations as low as 5 mg/L as N (Ward et al., 2018). In FY19, nitrate + nitrite as nitrogen (N) was detected in 41 samples (52%), with 14 samples (18%) above 5 mg/L, and five samples (6%) exceeding 10 mg/L. Figure 5 is a map showing concentrations of nitrate + nitrite as N measured in FY19. The highest individual and median nitrate concentrations were reported in wells drawing water from alluvial aquifers in FY19, as is the case when nitrate concentrations from ambient monitoring records since 2002 are compared (Figure 6). For those public systems with high nitrate concentrations in their source waters, blending of multiple wells and/or treatment was used to meet compliance standards.

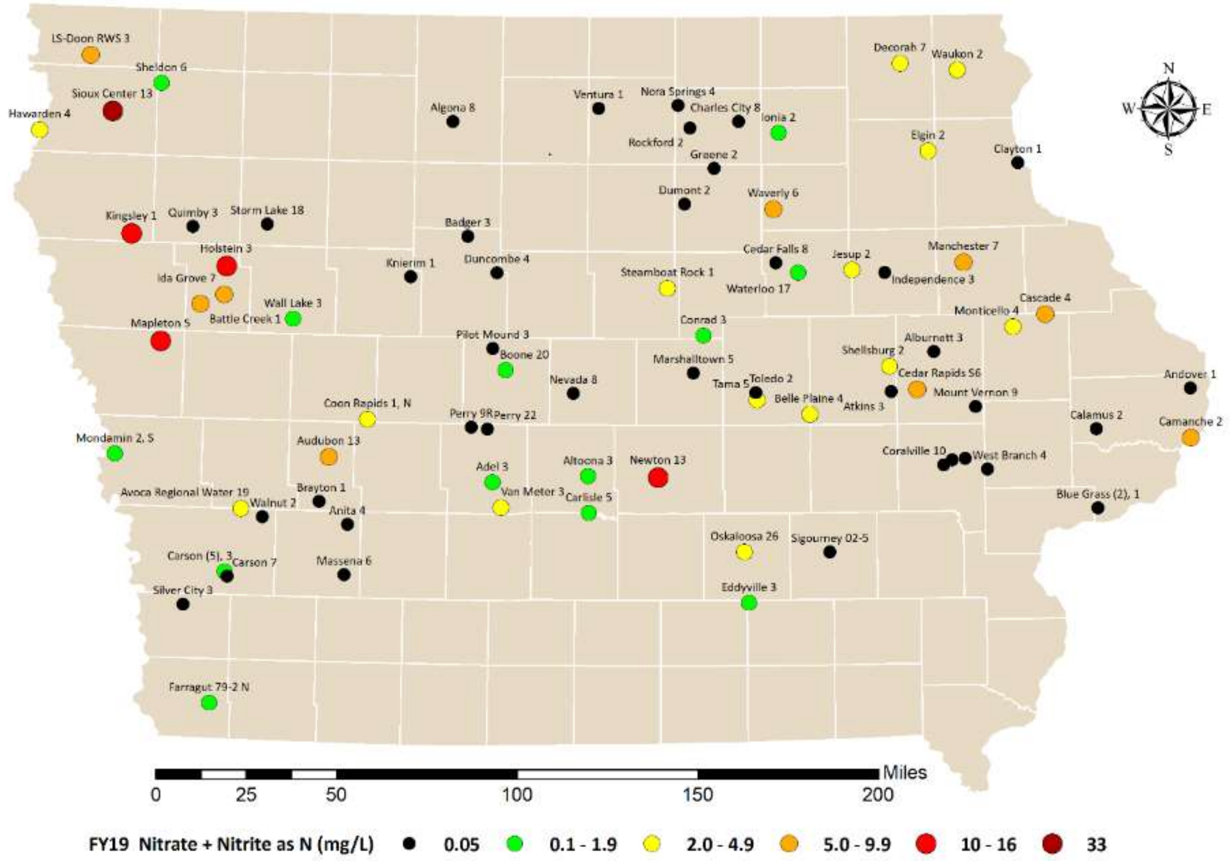


Figure 5. Nitrate + Nitrite as N concentrations in FY19 groundwater samples.

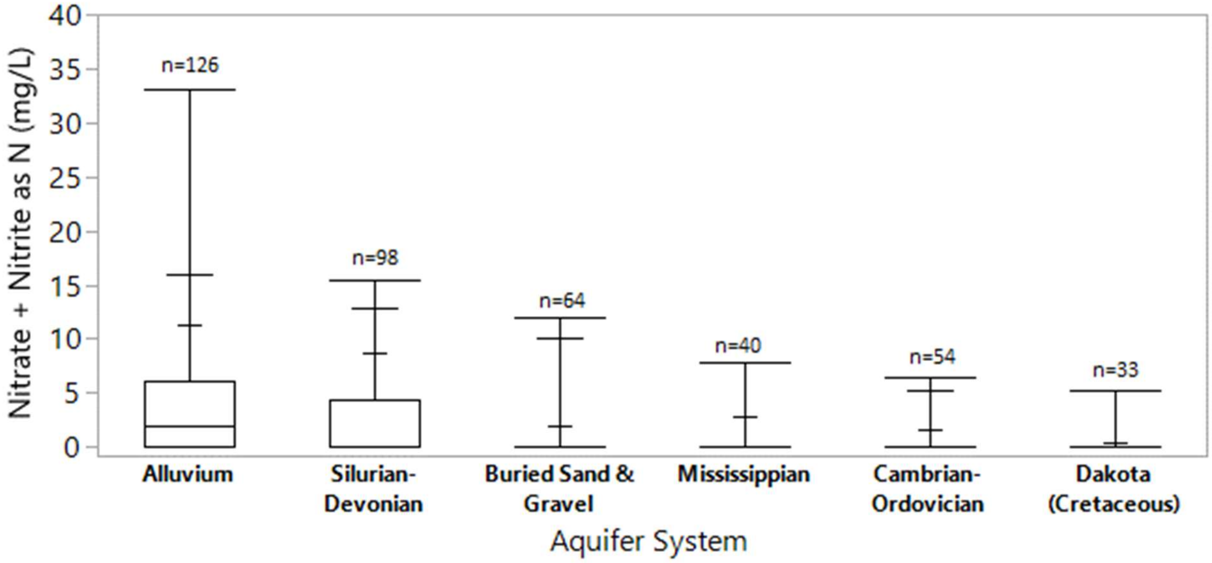


Figure 6. Quartile boxplots showing distributions of nitrate + nitrite as N concentrations in ambient groundwater monitoring program wells (2002-FY2019) by aquifer system. To avoid bias from frequently monitored wells, only the most recent result from each of 415 public water supply wells were included in this analysis. Reported concentrations below reporting limits were assigned values of half the reporting limit. Wells drawing water from more than one major aquifer system, and the two wells representing the Pennsylvanian aquifer system were excluded from this analysis.

Nitrate trends

Historical records from the 14 wells with nitrate concentrations above 5 mg/L in FY19 were analyzed to evaluate trends in nitrate concentrations. Only nitrate + nitrite as N concentrations collected as part of the ambient groundwater monitoring program and analyzed by the State Hygienic Laboratory (SHL) were used for this analysis. The number of records available in the AQuIA database (starting in 2002) for these wells ranged from five to twelve. Nine of these wells had data available from both the 2002-2006 and 2012-2019 periods, while the remaining five wells only had results available since 2012. No samples were taken from these wells for the period from 2007 – 2011. All of the wells included in this analysis were alluvial with the exception of Manchester 7, Cascade 4, and Waverly 6, which draw water from the Silurian-Devonian system in NE Iowa. Available nitrate concentration data were fit with linear trendlines (Figure 7), and the results of that trend analysis are reported in Table 3.

Results of this analysis show nitrate concentrations increasing for 13 of the 14 wells at rates from -0.09 to 4.15 mg/L/year. Some of these increases may be underestimated because samples from 2002 to 2006 and 2012 were collected during the summer months when nitrate levels are generally highest in shallow groundwater, while samples from 2013 to 2019 were collected during winter months when nitrate levels are often lower in shallow groundwater. Manchester 7 was the only well that showed decreasing concentrations of nitrate since 2002.

Sioux Center's well 13 showed the highest rate of increase and the highest measured nitrate concentration in FY19. Monthly testing by IDNR's Contaminated Sites Program as part of a Source Water Protection evaluation between 2006 - 2008 show levels of nitrate in Sioux Center well 13 ranging from below detection to 16 mg/L. When combined with the more recent ambient monitoring, these records show that nitrate concentrations increasing, but at a lower rate (1.54 mg/L per year). Monthly tests of pre-treatment nitrate concentrations at some of these wells are available within the DNR's SDWIS database and could be used to supplement and improve nitrate trend analyses in the future.

Table 3 also shows the predicted nitrate value for 2030 based on the linear trends. Nitrate concentrations in five of these wells exceeded 10 mg/L in FY19, and these analyses suggest that, if the rate of change is not altered, average nitrate at another three wells will exceed the standard by 2030. Changes to land-use practices, soil processes, and weather could alter the trajectories of nitrate concentrations over the next 10 years. The predictions listed in Table 3 should be used with caution and are, perhaps, most valuable for the purposes of illustrating the importance of understanding both the current nitrate levels AND the rate of change for prioritization and evaluation of source water protection efforts.

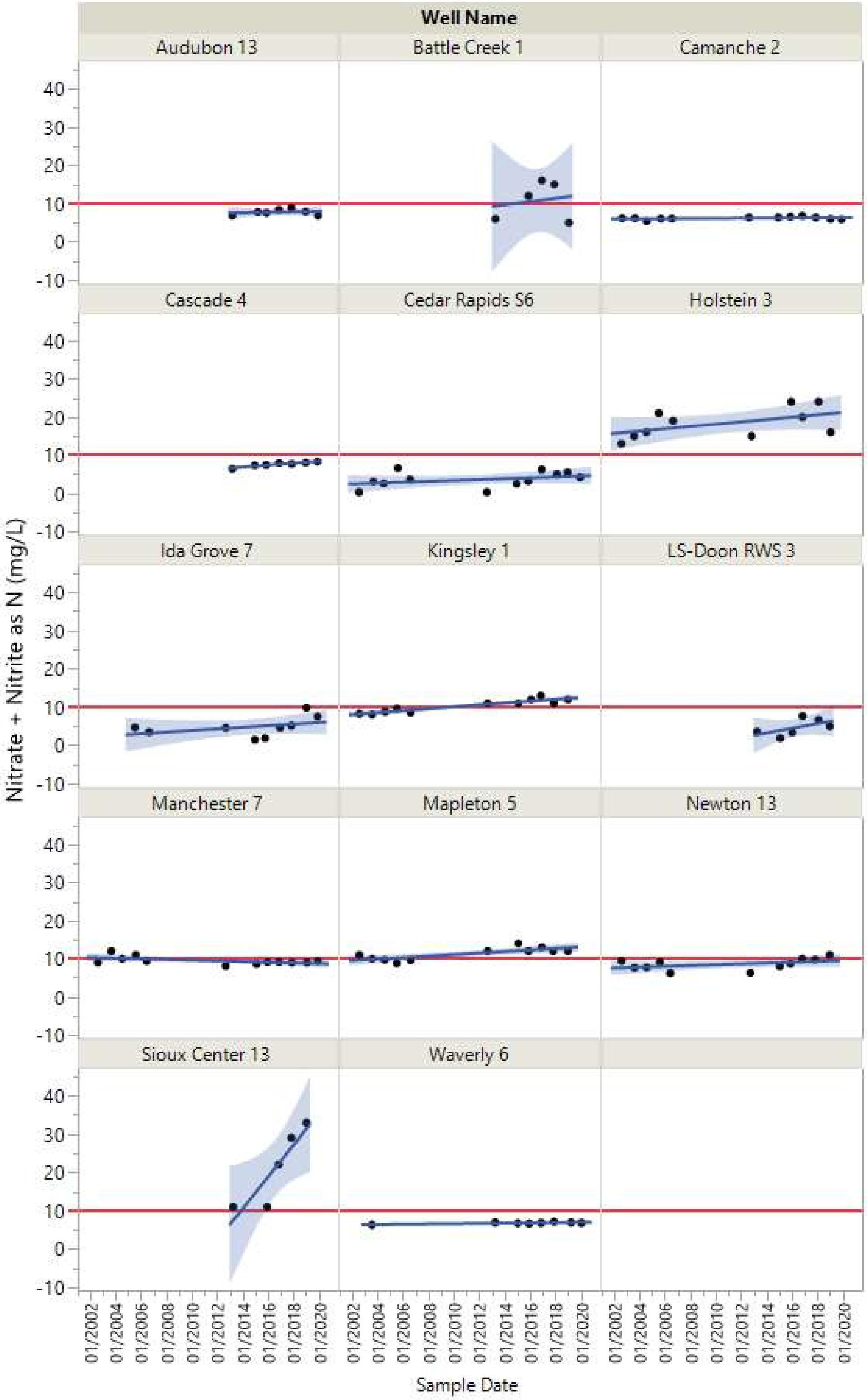


Figure 7. Nitrate + nitrite as N concentrations for selected wells from 2002-2020. Blue shaded areas indicate 95% confidence limits of trendlines.

Table 3. Summary of linear analysis of nitrate + nitrite as N concentrations in selected wells since 2002.

Well Name	Aquifer System	N	First Year	Slope	y-intercept (1/1/1900 0:00)	r2	RMSE	Change in Nitrate + Nitrite as N (mg/L yr^{-1})	2030 predicted Nitrate + Nitrite as N (mg/L)
Audubon 13	Alluvium	7	2013	0.000171	0.459	0.039	0.79	0.06	8.6
Battle Creek 1	Alluvium	5	2013	0.001155	-38.379	0.034	5.75	0.42	16.5
Camanche 2	Alluvium	12	2002	0.000056	3.926	0.139	0.35	0.02	6.6
Cascade 4	Silurian-Devonian	7	2013	0.000689	-21.819	0.893	0.22	0.25	10.9
Cedar Rapids S6	Alluvium	12	2002	0.000317	-9.332	0.139	1.99	0.12	5.7
Holstein 3	Alluvium	10	2002	0.000841	-15.653	0.271	3.52	0.31	24.3
Ida Grove 7	Alluvium	9	2005	0.00057	-19.144	0.174	2.53	0.21	7.9
Kingsley 1	Alluvium	11	2002	0.00068	-17.242	0.863	0.66	0.25	15.0
LS-Doon RWS 3	Alluvium	6	2013	0.001673	-66.396	0.335	1.99	0.61	13.0
Manchester 7	Silurian-Devonian	12	2002	-0.00025	19.596	0.313	0.93	-0.09	7.8
Mapleton 5	Alluvium	11	2002	0.000538	-10.532	0.611	1.05	0.20	15.0
Newton 13	Alluvium	11	2002	0.0003	-3.613	0.208	1.43	0.11	10.6
Sioux Center 13	Alluvium	5	2013	0.011381	-463.40	0.807	5.13	4.15	77.0
Waverly 6	Silurian-Devonian	8	2003	0.000097	2.679	0.597	0.16	0.04	7.3

Differences in the variability in nitrate concentrations reflect differences in hydrological settings of these wells. In some settings, like shallow alluvial systems, water may flow from the surface to the well within days to weeks. In unconfined bedrock wells, some of the groundwater may have flowed underground for hundreds of years before reaching the well. In the Silurian-Devonian aquifer system in Iowa, well water is often a mixture of ages with higher concentrations of nitrate in the upper parts of the aquifer mixing with lower concentrations in older water at the base of the aquifer. The variability of nitrate in a well may also have implications for the speed of success from nutrient reduction efforts. Wells with high nitrate variability indicate rapid response to precipitation and also suggest that reductions in nitrogen inputs are likely to lead to relatively fast reductions in nitrate concentrations in groundwater. In contrast, watershed protection efforts around wells with low variability in nitrate concentrations may be slower to respond.

One measure of variability is the root mean square error (RMSE), which is defined as the standard deviation of the residuals between the measured value and the line of best fit. The highest RMSE values were seen in Battle Creek 1, Holstein 3, and Sioux Center 13; three alluvial wells in NW Iowa (Table 3). The RMSE for these three sites was greater than 3.5. For wells with highly variable concentrations, it is unlikely that a single sample per year is an accurate representation of the water quality. These wells have been shown to respond quickly to recharge events, leading to large swings in nitrate concentrations over short periods of time.

Potential sources of nitrate in Iowa's groundwater include commercial fertilizer, manure, wastewater, soil organic matter, and leaky septic systems. Linear relationships between fertilizer application rates and groundwater nitrate concentrations at Big Spring in Iowa's karst region were described by Hallberg et al. (1983). Linear relationships between percentage of watershed acres planted in row-crops and stream nitrate in Iowa were also observed by Schilling and Libra (2000). Statewide, the number of acres planted in corn has risen since 2000, while the number of acres planted in soybeans has declined (Nowatzke and Benning, 2020). Continuous corn rotations require more nitrogen fertilization than corn-soybean rotations because soybeans are able to fix their own nitrogen from the atmosphere. These land-use changes may explain the increased nitrogen losses to groundwater in unconfined aquifer systems, although the timing of the groundwater response may be faster or slower depending on local hydrological conditions, and each well represents a different mixture of nitrogen sources.

While a linear analysis appears to be sufficient to describe change in nitrate concentrations over the short term (20 years), longer term nitrate response to status quo land use or significant nitrate reduction efforts would theoretically lead to a plateau in nitrate concentrations or a parabolic response, respectively. One useful tool for visualizing such changes in concentrations is the US Geological Survey's GAMACCT tool (https://ca.water.usgs.gov/projects/gamactt/).

Nitrogen dynamics are influenced by nitrogen sources, precipitation patterns, redox conditions in the subsurface, groundwater travel times, well construction and operation, and many other factors. The ambient groundwater monitoring program only samples a small percentage of Iowa's public water supply wells each year and an even smaller percentage of wells have sufficient long-term water quality data to support trend analyses. Therefore, it is not possible to reliably use ambient groundwater monitoring records to predict nitrate concentrations at untested locations, nor is the ambient groundwater quality monitoring dataset statistically representative of statewide aquifer trends. However, as this analysis shows, we can get a sense of the magnitude of the changes at individual wells across our state. As communities increasingly focus on efforts to reduce nitrate in their source waters, they will benefit from good historical records and a clear understanding of the hydrology of their systems.

Researchers have developed a predictive model for past nitrate concentrations in private wells in Iowa with good success based on well depth, distance to sinkholes, and other factors, but without stratigraphic or well construction information (Wheeler et al., 2015). More monitoring data, both spatially and temporally, from wells with good construction and geologic records would be necessary to accurately assess statewide trends in nitrate by aquifer. In addition, a better understanding of variability of nitrate concentrations with depth in the Silurian-Devonian aquifer system would benefit efforts to predict long-term responses to land use changes.

2 - Using isotopes to help identify sources of nitrate in groundwater:

Communities working to reduce nitrate in their source waters are increasingly looking to understand not only where on the landscape the nitrate could be coming from, but also what sources have contributed nitrate to their wells. Determining which sources have impacted an individual well or drinking-water system can be challenging because of effects of variable weather and climate, complex underground flow pathways, soil processes, mixing of waters, and changes in land-use over time. Sources of nitrate include commercial nitrogen-based fertilizers, manure, human waste, soils, and precipitation. One tool available to help us distinguish between these sources is to measure the isotopic ratios of nitrogen and oxygen that make up the nitrate molecules. Interpreting the results of these tests can be complicated, and should be put into context with information about the geology, well construction and operation, land-use history, and supporting water quality records.

Each nitrate molecule (NO_3^-) contains one atom of nitrogen (N) bonded to three atoms of oxygen (O). There are only a few stable isotopes of oxygen and nitrogen that occur in the environment. Each isotope has a different number of neutrons, which don't affect the charge of the atom, but do affect the mass of an atom. Atoms with more neutrons are heavier, like ^{18}O and ^{15}N, and isotopes with fewer neutrons are lighter, like ^{16}O and ^{14}N. To compare various sources of nitrate, we use isotopic ratios of oxygen ($^{18}O/^{16}O$) and nitrogen ($^{15}N/^{14}N$), relative to standards. Oxygen isotope ratios ($^{18}O/^{16}O$) are compared to the ratio of ^{18}O to ^{16}O in standard mean ocean water (SMOW), and reported as $\delta^{18}O_{NO3}$ ‰. Nitrogen isotopic ratios are compared to the average ratio of ^{15}N to ^{14}N in the atmosphere, and reported as $\delta^{15}N_{NO3}$ ‰. For both isotope pairs, a reported value of 1 is the equivalent to a measured ratio 1000 times higher than the standard.

Isotopic ratios increase (get heavier) or decrease (get lighter) due to various natural and industrial processes. Based on our understanding of physical and biological processes and results from known sources, we can predict the ranges of values of N and O isotopic ratios for various sources of nitrate. Carol Kendall (from the US Geological Survey in Menlo Park, CA) and Ramon Aravena (from the University of Waterloo, Canada) published a diagram that shows the characteristic isotopic ranges of nitrate sources (Figure 8). This diagram also shows how the process of denitrification in the subsurface can increase $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$. Denitrification occurs under anoxic (low oxygen) conditions, when microorganisms convert nitrate to nitrite, then to nitrous oxide (a gas).

Figure 8 shows that oxygen isotope ratios resulting from conversion of ammonium to nitrate in soils (nitrification) are expected to fall within the range of -15 to 15 $\delta^{18}O_{NO3}$ ‰. Since most nitrogen is applied to cropland in the form of ammonium (in commercial fertilizer and manure) or is deposited on the ground by rainfall, we expect the majority of groundwater samples to fall within this range. There are some fertilizer formulations that contain nitrate instead of, or in addition to, ammonium. These sources are likely to have higher $\delta^{18}O_{NO3}$ values between 15 and 25 ‰.

Figure 8 also shows how isotopes of nitrogen can sometimes help distinguish between leaching of nitrate from application of commercial ammonia-based fertilizers or precipitation from animal or human waste. Nitrate from manure and septic waste typically has heavier isotopic nitrogen signatures (ranging from 0 to 25 $\delta^{15}N_{NO3}$ ‰) than nitrate derived from ammonia-based chemical fertilizers, which typically ranges from -10 to 5 $\delta^{15}N_{NO3}$ ‰. Unfortunately, these ranges overlap, so that water samples between 0 – 5 $\delta^{15}N_{NO3}$ ‰ could be from either source. To complicate matters, nitrate derived from ammonium in soils has had reported values between 2 – 8 $\delta^{15}N_{NO3}$ ‰.

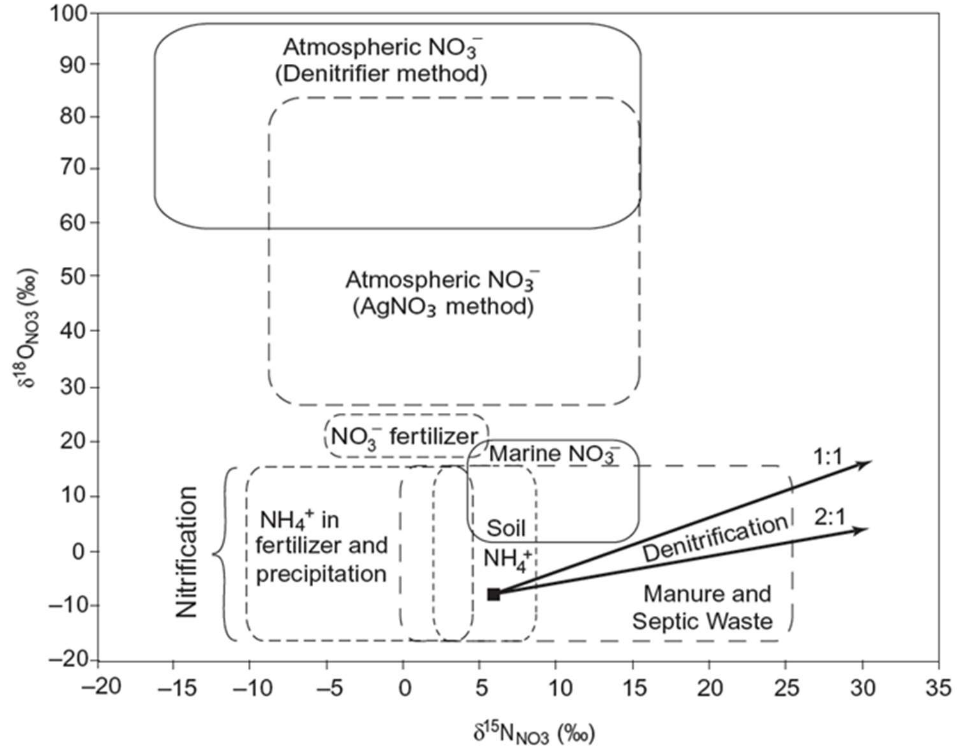


Figure 8. Typical ranges of oxygen and nitrogen isotope rations for various sources of nitrate in groundwater (from Kendal et al., 2007).

In FY19, samples were collected from 40 wells from 16 communities for nitrogen and oxygen isotopic analyses. Sampling was targeted towards communities reporting average nitrate concentrations above 5 mg/L as N. Specific wells were selected in cooperation with municipal water supply operators based on local knowledge and historical monitoring records. Samples were submitted to the Nebraska Water Sciences Laboratory and analyzed using an azide reduction and trace gas preconcentrator method to measure the ratios of ^{18}O to ^{16}O ($\delta^{18}O$) and ^{15}N to ^{14}N ($\delta^{15}N$) from nitrate. Samples from four wells did not contain sufficient nitrate (>0.01 mg/L nitrate + nitrite as N) to be processed for isotopes.

Isotope results and corresponding nitrate concentrations for 36 individual wells sampled during FY19 are plotted in Figure 9. Thirty-three (92%) of these samples fell between -2 to 15 δ^{18}O ‰, indicating that most of the nitrate originated from ammonia, either commercial fertilizer, precipitation, soil ammonia, manure, or septic waste. The other three samples (8%) had δ^{18}O values just above 15 ‰, possibly indicating contributions from a nitrate-based commercial fertilizer source.

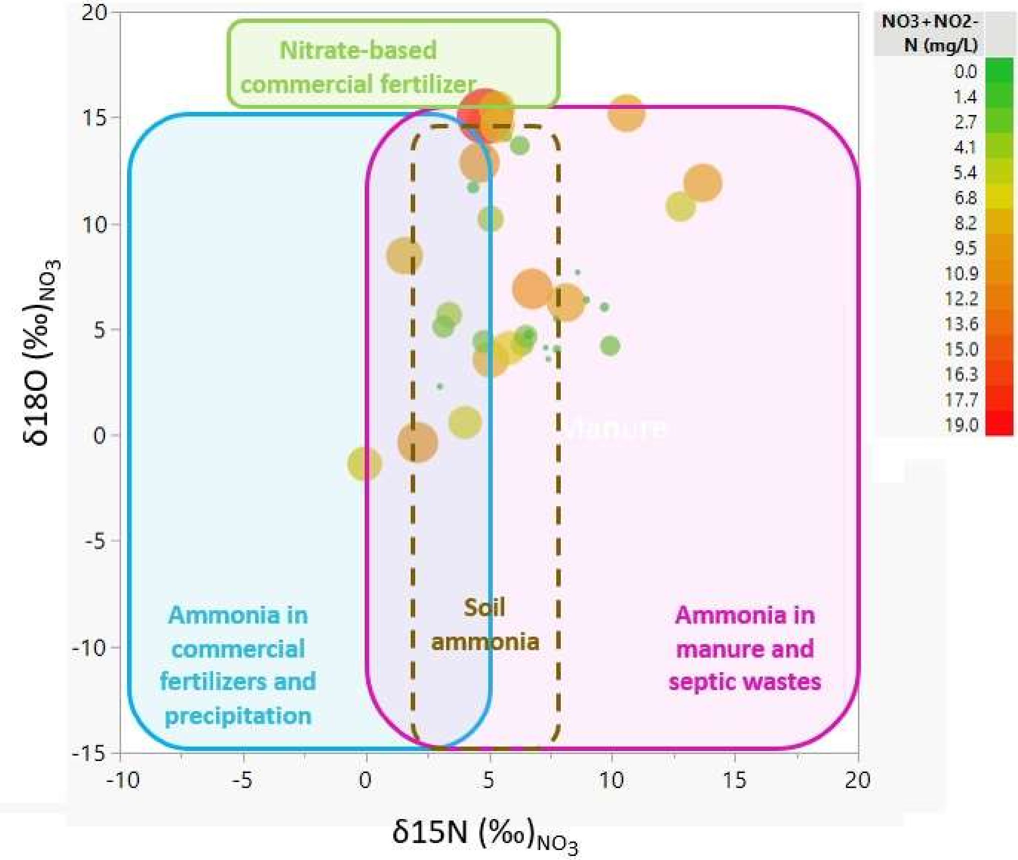


Figure 9. Nitrogen (δ15N) and oxygen (δ18O) isotopic ratios for groundwater samples collected in FY19. Size and color of points correspond to reported nitrate + nitrite as N concentrations. Colored boxes show areas of the plot characteristic of different sources of nitrate in groundwater as published by Kendall et al., 2007.

Values of δ^{15}N above 8 ‰ suggest that the nitrate in these samples was most likely derived from manure or septic waste (28% of samples). It is also possible that denitrification processes could have increased δ^{15}N values under low oxygen conditions. Significant denitrification is unlikely in samples with high nitrate concentrations, but collection of more data related to redox conditions would be necessary to completely rule out the effects of denitrification on these samples. One sample had a reported value of δ^{15}N below 0 ‰, suggesting that the nitrate was derived primarily from an ammonia-based commercial fertilizer or precipitation. Reported concentrations of ammonia in precipitation in Iowa rarely exceed 1 mg/L (National Atmospheric Deposition Program), therefore, it is unlikely that precipitation was the sole source of nitrogen for this sample that contained 7.42 mg/L nitrate + nitrite as N. Most (69%) samples contain δ^{15}N between 0 – 8 ‰, the area of overlap for which the primary source of the nitrate is not distinguishable. Samples that fall in this range could be derived from ammonia in commercial fertilizer, precipitation, soils, manure or septic waste, or a combination of these sources. For the seven samples with relatively low concentrations of nitrate (<1 mg/L), and δ^{15}N values between 2 – 8 ‰, it is possible that all of the nitrate was soil-derived.

It is important to understand that nitrate in each well may result from activities on the landscape anywhere from days to decades before it is detected in groundwater. Even when the isotopic results plot to the far right (manure or septic) or the far left (ammonia-based commercial fertilizer or precipitation) of the diagram, it is possible that a mixture of sources are present. In addition, the sources of nitrate may change seasonally, and from year to year, complicating the interpretation of these results. Denitrification under low oxygen conditions may also impact results. To better understand the effects of this process, more frequent sampling (a minimum of 4 quarters), and characterization of the redox conditions in the well would be necessary. Isotope ratio results for individual wells tested as part of the ambient groundwater monitoring program in FY18 and FY19 are listed in Appendix A along with preliminary interpretations based on the single sample collected for analysis of both nitrate concentrations and isotopic ratios. However, these results should be used with caution for the reasons listed above.

3 – Water quality in unpumped Silurian-Devonian monitoring wells

The IIHR-Iowa Geological Survey (IGS) maintains six dedicated monitoring wells that draw water from the Silurian-Devonian aquifer system in Linn and Jones counties (mapped in Figure 10 and listed in Table 4). Unlike the majority of the ambient groundwater monitoring well network, these wells are not municipal water supply wells and are not regularly pumped. Static water levels in four of these wells have been monitored by IGS and the US Geological Survey (USGS) since they were drilled by the Geological Survey Bureau (now IGS) in the 1970's. The two Westfield wells have had sporadic static water level measurements from 2003 to 2011, then more regularly since 2011.

Table 4. Dedicated monitoring wells sampled in FY19. Historical records and well information can be found using the ID's provided.

Well Name	WNumber (GEOSAM ID)	STORET ID (IDNR-AQuIA)	USGS ID (USGS-NWIS)	Depth (ft)	Confining Material	Year Drilled
White Oak Ck 25	23891	35530001	415808091160501	517	17 ft Till	1976
Marion 23	23785	35570011	420300091325801	481	105 ft Till	1976
Alice 11	23268	35570009	421149091403301	435	22 ft Till	1973
Ely NW 21	23766	35570010	415343091360101	401	31 ft till+clay	1976
Westfield 1	56819	35570001		455	26 ft clay+till	2003
Westfield 2	57355	35570002		200	40 ft till+shale	2003

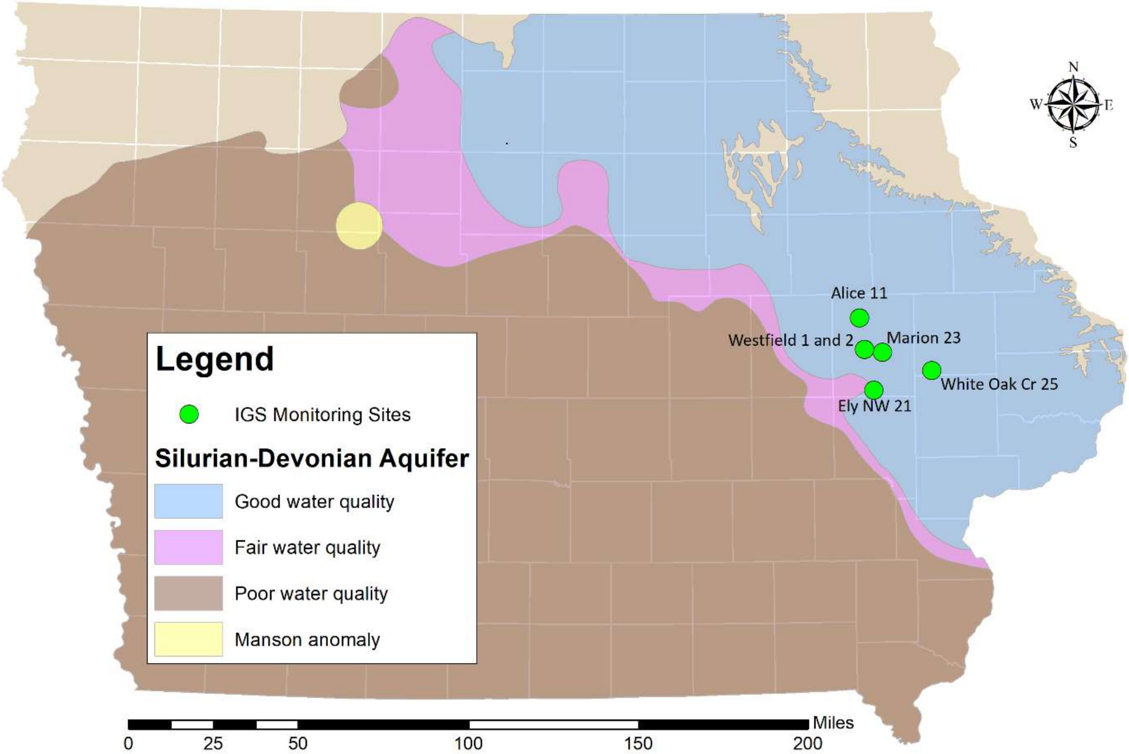
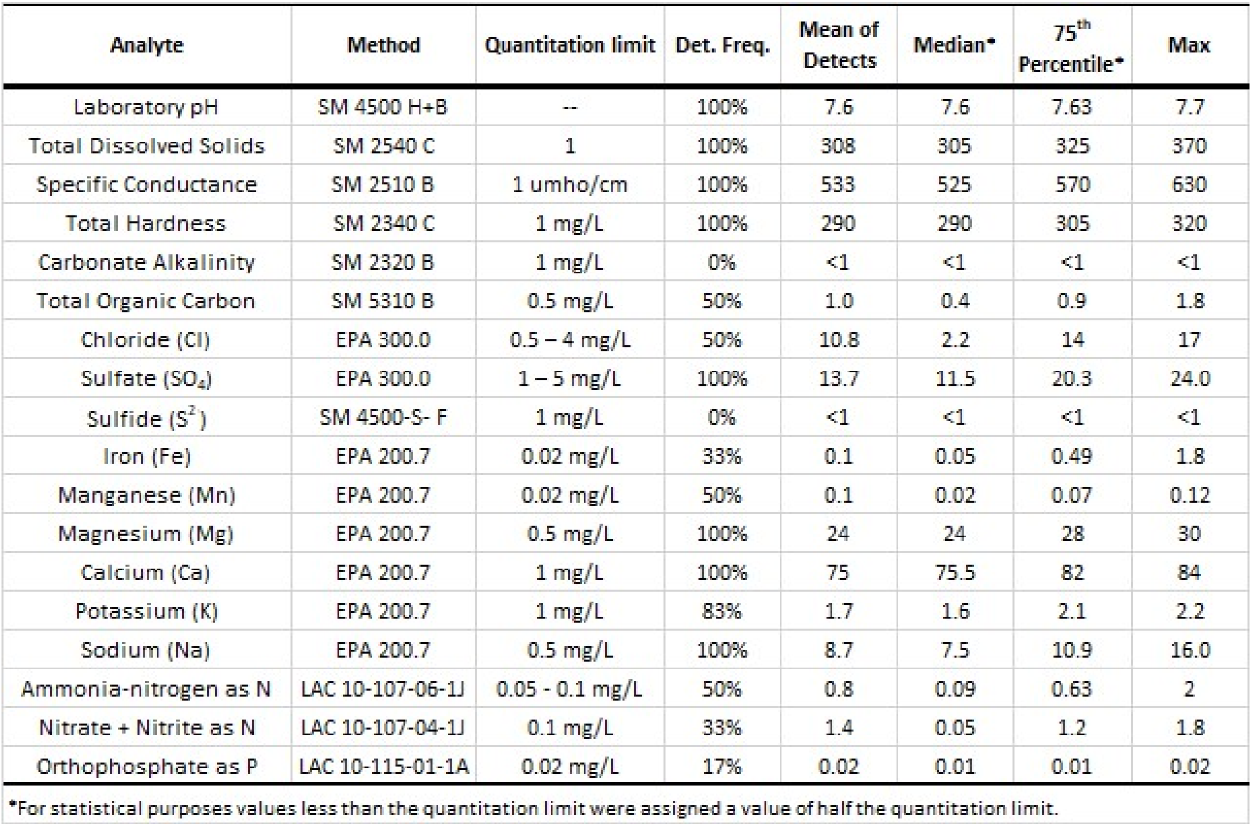


Figure 10. Monitoring wells maintained by the Iowa Geological Survey and sampled for water quality in FY19.

In partnership with IGS, IDNR supported water quality monitoring at these locations in FY19. Samples were collected by IGS staff between December 19, 2018, and January 8, 2019. Table 5 contains a summary of the results for these six wells. While general water quality parameters are similar to pumped Silurian-Devonian wells, these wells appear to be less impacted by nitrate (max concentration = 1.8 mg/L as N) than nearby pumped municipal wells using the Silurian-Devonian aquifer system, such as Hiawatha 4, Shellsburg 2, Mechanicsville 2, and Mount Vernon 2, which have all had reported nitrate + nitrite values greater than 2 mg/L as N; however, it is not possible to directly compare samples taken months to years apart. Further analysis and more synchronous sampling of nearby pumped wells will be necessary before the effects of pumping, recharge, land use changes, and other factors can be evaluated.

Water quality data for these six dedicated wells from FY19 can be accessed via the AQuIA website. https://programs.iowadnr.gov/aquia/ Choose "Go directly to a site" in the lower left-hand corner, then enter the STORET ID, or click on "Data Search," then choose the Iowa GW facility from the drop-down list, then select the wells by name or by ID. AQuIA also contains water quality data for the two Westfield wells from 2003 and 2006. No major changes in water quality were observed in comparison to historical records at these locations.

Table 5. Summary of results of FY19 sampling for six dedicated monitoring wells representing un-pumped conditions in the Silurian-Devonian aquifer system.



Analyte	Method	Quantitation limit	Det. Freq.	Mean of Detects	Median*	75th Percentile*	Max
Laboratory pH	SM 4500 H+B	--	100%	7.6	7.6	7.63	7.7
Total Dissolved Solids	SM 2540 C	1	100%	308	305	325	370
Specific Conductance	SM 2510 B	1 umho/cm	100%	533	525	570	630
Total Hardness	SM 2340 C	1 mg/L	100%	290	290	305	320
Carbonate Alkalinity	SM 2320 B	1 mg/L	0%	<1	<1	<1	<1
Total Organic Carbon	SM 5310 B	0.5 mg/L	50%	1.0	0.4	0.9	1.8
Chloride (Cl)	EPA 300.0	0.5 – 4 mg/L	50%	10.8	2.2	14	17
Sulfate (SO_4)	EPA 300.0	1 – 5 mg/L	100%	13.7	11.5	20.3	24.0
Sulfide (S^{2-})	SM 4500-S- F	1 mg/L	0%	<1	<1	<1	<1
Iron (Fe)	EPA 200.7	0.02 mg/L	33%	0.1	0.05	0.49	1.8
Manganese (Mn)	EPA 200.7	0.02 mg/L	50%	0.1	0.02	0.07	0.12
Magnesium (Mg)	EPA 200.7	0.5 mg/L	100%	24	24	28	30
Calcium (Ca)	EPA 200.7	1 mg/L	100%	75	75.5	82	84
Potassium (K)	EPA 200.7	1 mg/L	83%	1.7	1.6	2.1	2.2
Sodium (Na)	EPA 200.7	0.5 mg/L	100%	8.7	7.5	10.9	16.0
Ammonia-nitrogen as N	LAC 10-107-06-1J	0.05 - 0.1 mg/L	50%	0.8	0.09	0.63	2
Nitrate + Nitrite as N	LAC 10-107-04-1J	0.1 mg/L	33%	1.4	0.05	1.2	1.8
Orthophosphate as P	LAC 10-115-01-1A	0.02 mg/L	17%	0.02	0.01	0.01	0.02

*For statistical purposes values less than the quantitation limit were assigned a value of half the quantitation limit.

The IGS Geosam database contains casing information, stratigraphy, and water level data for these sites. https://www.iihr.uiowa.edu/igs/geosam/home Click on the "Text-Based" Search, then input the Geosam ID in the WNumber field.

The USGS' National Water Information System (NWIS) contains water quality information for Ely NW 21, Alice 11, and water level data for White Oak Ck, Marion 23, Alice 11, and Ely NW 21 from 1975 to 2013. https://nwis.waterdata.usgs.gov/nwis Check the "Site Number" box on the Site Selection Criteria page, then hit submit. Input the USGS ID and then scroll to the bottom to select "Table of data" from the Output Options and hit submit.

Conclusions:

Ambient groundwater quality monitoring has made it possible to better understand the occurrence of both natural and anthropogenic contaminants in Iowa. The FY19 data confirm that manganese and nitrate occur above levels of concern in alluvial aquifers, though rarely in the same wells, and that concentrations of nitrate have risen in several wells since 2002. In some cases, isotopes of nitrogen and oxygen can help us to distinguish between dominant sources of nitrate, but these results should be interpreted in the context of additional hydrological and geochemical information. More frequent sampling, especially in shallow alluvial settings, will be necessary to evaluate nitrate trends and sources. Additionally, careful assessment of redox conditions should be considered for future monitoring efforts in order to better understand geochemical processes influencing municipal well water quality.

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APPENDIX A

Well or site name	Sample Date	NO3+NO2-N (mg/L)	det limit (mg/L)	$\delta 15N_{NO3}$ (‰)	$\delta 18O_{NO3}$ (‰)	Ammonia in Commercial Fertilizer or	Soil Ammonia	Ammonia in Manure or Septic Waste	Nitrate Fertilizer	Interpretation
Adel 3	11/28/2017	0.03	0.01	1.59	4.93	🟦		🟪		Possible mixture of sources
Algona 8	12/5/2017	0.01	0.01							Insufficient nitrate for isotopic analyses
Audubon 13	12/12/2017	4.83	0.01	6.83	1.48		🟫	🟪		Possible mixture of sources
Avoca Red Water 19	12/4/2017	0.30	0.01	0.48	-9.24	🟦		🟪		Possible mixture of sources
Battle Creek 3	11/27/2017	9.90	0.01	0.47	1.66	🟦		🟪		Possible mixture of sources (more likely to be commercial fertilizer)
Belle Plaine 4	2/13/2018	2.27	0.01	10.62	4.34			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Boone 13	11/20/2017	1.53	0.01	5.90	13.12		🟫	🟪		Possible mixture of sources
Boone 20	11/20/2017	1.95	0.01	2.31	3.58	🟦		🟪		Possible mixture of sources
Bristow 2	1/9/2018	4.70	0.01	-7.03	-1.16	🟦				Dominant source is most likely ammonia from commercial fertilizer (nitrate too high to be precipitation-derived)
Brookhill 1	12/12/2018	0.04	0.01							Insufficient nitrate for isotopic analyses
Camanche 2	12/12/2017	3.72	0.01	15.05	5.52			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Carlisle 5	5/1/2018	0.82	0.01	5.11	4.92		🟫	🟪		Possible mixture of sources
Carson (5), 3	11/28/2017	0.31	0.01	3.85	1.80	🟦	🟫	🟪		Possible mixture of sources
Cascade 4	11/27/2017	8.74	0.01	4.02	-1.79	🟦	🟫	🟪		Possible mixture of sources
Cedar Falls 10	3/19/2019	0.91	0.01	4.36	11.69	🟦	🟫	🟪		Possible mixture of sources
Cedar Falls 8	3/19/2019	0.00	0.01							Insufficient nitrate for isotopic analyses
Cedar Falls 9	11/27/2017	11.20	0.01	1.31	-3.83	🟦		🟪		Possible mixture of sources
Cedar Falls 9	3/19/2019	0.52	0.01	4.93	13.47	🟦	🟫	🟪		Possible mixture of sources
Cedar Rapids S6	11/27/2017	3.13	0.01	8.96	1.12			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Conrad 3	11/27/2017	1.24	0.01	3.87	2.63	🟦	🟫	🟪		Possible mixture of sources
Correctionville 1W	1/8/2018	13.20	0.01	-0.91	1.01	🟦				Dominant source is most likely ammonia from commercial fertilizer (nitrate too high to be precipitation-derived)
Decorah 7	11/20/2017	3.78	0.01	5.35	9.44		🟫	🟪		Possible mixture of sources
Dow City 2	12/19/2018	0.56	0.01	6.62	4.75		🟫	🟪		Possible mixture of sources
Dow City 3	12/19/2018	0.13	0.01	7.32	4.13		🟫	🟪		Possible mixture of sources
Dunlap 1	12/12/2018	5.75	0.01	12.80	10.80			🟪		Dominant source is most likely ammonia in manure or septic waste
Dunlap 3	12/12/2018	6.84	0.01	5.83	4.11		🟫	🟪		Possible mixture of sources
Dunlap 4	12/12/2018	3.20	0.01	6.50	4.65		🟫	🟪		Possible mixture of sources
Dunning's Spring	11/6/2017	12.16	0.01	0.92	3.98	🟦		🟪		Possible mixture of sources
Eddyville 3	11/28/2017	2.20	0.01	2.65	-3.45	🟦	🟫	🟪		Possible mixture of sources
Elgin 2	1/22/2018	6.50	0.01	6.29	2.92		🟫	🟪		Possible mixture of sources
Elliot 1	12/11/2018	0.46	0.01	7.77	4.05			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Elliot 2	12/11/2018	0.18	0.01	7.42	3.59		🟫	🟪		Possible mixture of sources
Farragut 79-2 N	12/5/2017	0.52	0.01	-3.45	-13.83	🟦				Dominant source is most likely ammonia from commercial fertilizer or precipitation
Griswold 3	1/7/2019	8.70	0.01	10.60	15.20			🟪	🟩	Possible mixture of sources
Griswold 4	1/7/2019	4.21	0.01	3.38	5.67	🟦	🟫	🟪		Possible mixture of sources
Griswold 5	1/7/2019	4.22	0.01	5.07	10.20		🟫	🟪		Possible mixture of sources
Hastings 1	1/14/2019	3.17	0.01	3.15	5.12	🟦	🟫	🟪		Possible mixture of sources
Holstein 1 (W567)	1/14/2019	0.00	0.01							Insufficient nitrate for isotopic analyses
Holstein 3	1/30/2018	24.11	0.01	7.37	5.14		🟫	🟪		Dominant source is most likely ammonia in manure or septic waste
Holstein 3	1/14/2019	7.61	0.01	4.81	14.76	🟦	🟫	🟪		Possible mixture of sources
Holstein 4	1/14/2019	19.04	0.01	4.84	15.05	🟦	🟫	🟪	🟩	Possible mixture of sources
Holstein 7	1/14/2019	8.33	0.01	1.57	8.47	🟦		🟪		Possible mixture of sources
Holstein 8	1/14/2019	2.37	0.01	6.25	13.67		🟫	🟪		Possible mixture of sources
Ida Grove 7	11/28/2017	4.03	0.01	2.38	-0.91	🟦		🟪		Possible mixture of sources
Jesup 2	11/27/2017	2.81	0.01	5.90	0.61		🟫	🟪		Possible mixture of sources
Kingsley 1	12/11/2017	12.59	0.01	17.52	5.00			🟪		Dominant source is most likely ammonia in manure or septic waste
Kingsley 3	12/11/2017	7.43	0.01	4.98	1.86	🟦	🟫	🟪		Possible mixture of sources
Kingsley 4	12/12/2017	0.02	0.01							Insufficient nitrate for isotopic analyses
Lyon Sioux RWS 12	1/29/2018	29.98	0.01	13.47	6.25			🟪		Dominant source is most likely ammonia in manure or septic waste
Lyon Sioux RWS 3	1/29/2018	15.83	0.01	4.57	0.07	🟦	🟫	🟪		Possible mixture of sources
Lyon Sioux RWS 4	1/29/2018	15.53	0.01	9.55	3.27			🟪		Dominant source is most likely ammonia in manure or septic waste

Well or site name	Sample Date	NO3+NO2-N (mg/L)	det limit (mg/L)	$\delta 15N_{NO3}$ (‰)	$\delta 18O_{NO3}$ (‰)	Ammonia in Commercial Fertilizer or Precipitation	Soil Ammonia	Ammonia in Manure or Septic Waste	Nitrate Fertilizer	Interpretation
Manchester 5	1/10/2018	13.50	0.01	-7.29	-3.93	🟦				Dominant source is most likely ammonia from commercial fertilizer (nitrate too high to be precipitation-derived)
Manchester 6	1/10/2018	15.50	0.01	-3.15	-1.49	🟦				Dominant source is most likely ammonia from commercial fertilizer or precipitation
Manchester 7	1/10/2018	10.40	0.01	-4.18	-1.55	🟦				Dominant source is most likely ammonia from commercial fertilizer (nitrate too high to be precipitation-derived)
Manchester 8	1/10/2018	8.74	0.01	-2.34	-0.19	🟦				Dominant source is most likely ammonia from commercial fertilizer or precipitation
Manchester Upper Spring	11/6/2017	15.82	0.01	1.07	3.77	🟦		🟪		Possible mixture of sources
Mapleton 5	11/27/2017	6.93	0.01	1.36	2.71	🟦		🟪		Possible mixture of sources
Massena 6	11/27/2017	0.003	0.01							Insufficient nitrate for isotopic analyses
Monticello 4	11/28/2017	3.72	0.01	3.64	-2.00	🟦	🟫	🟪		Possible mixture of sources
Monti-View 1	12/10/2018	10.10	0.01	6.77	6.90		🟫	🟪		Dominant source is most likely ammonia in manure or septic waste
Monti-View 2	12/10/2018	3.15	0.01	6.35	4.27		🟫	🟪		Dominant source is most likely ammonia in manure or septic waste
Moville 6 (Local 5)	11/28/2017	5.13	0.01	5.30	-0.63		🟫	🟪		Possible mixture of sources
Neola 4	1/28/2019	7.42	0.01	-0.05	-1.37	🟦				Dominant source is most likely ammonia from commercial fertilizer (nitrate too high to be precipitation-derived)
Newton 13	11/27/2017	2.15	0.01	0.92	3.70	🟦		🟪		Possible mixture of sources
Osage 2	1/7/2019	2.43	0.01	9.93	4.21			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Oskaloosa 26	12/18/2017	0.68	0.01	11.05	-2.15			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Pint's Subdivision 1	9/27/2017	6.77	0.01	8.30	8.48			🟪		Dominant source is most likely ammonia in manure or septic waste
Plainfield 1	1/9/2018	6.19	0.01	-2.74	-0.81	🟦				Dominant source is most likely ammonia from commercial fertilizer (nitrate too high to be precipitation-derived)
Remsen 8	4/16/2015	14.40	0.01	11.26	12.64			🟪		Dominant source is most likely ammonia in manure or septic waste
Rick Valley 4	12/10/2018	8.79	0.01	8.14	6.25			🟪		Dominant source is most likely ammonia in manure or septic waste
Rock Valley 3	12/10/2018	8.25	0.01	5.08	3.56		🟫	🟪		Possible mixture of sources
Rock Valley 6	12/10/2018	9.03	0.01	13.70	11.90			🟪		Dominant source is most likely ammonia in manure or septic waste
Saints Ave Apts 1	3/4/2019	10.23	0.01	2.10	-0.36	🟦		🟪		Possible mixture of sources
Sheldon 6	11/27/2017	0.11	0.01							Insufficient nitrate for isotopic analyses
Shellsburg 2	12/4/2017	2.09	0.01	8.58	4.81			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Sioux Center 1	12/4/2017	15.66	0.01	16.99	5.72			🟪		Dominant source is most likely ammonia in manure or septic waste
Sioux Center 11	12/4/2017	8.62	0.01	7.94	3.49			🟪		Dominant source is most likely ammonia in manure or septic waste
Sioux Center 13	12/4/2017	21.55	0.01	16.88	4.88			🟪		Dominant source is most likely ammonia in manure or septic waste (known livestock source)
Sioux Center 2	12/4/2017	4.15	0.01	-2.07	-6.34	🟦				Dominant source is most likely ammonia from commercial fertilizer (nitrate too high to be precipitation-derived)
Spring Branch	11/6/2017	13.86	0.01	1.27	4.67	🟦		🟪		Possible mixture of sources
St. Ansgar 2	1/9/2018	0.02	0.01							Insufficient nitrate for isotopic analyses
Steamboat Rock 1	1/9/2018	1.87	0.01	-1.23	-3.52	🟦				Dominant source is most likely ammonia from commercial fertilizer or precipitation
Tama 5	12/13/2017	3.06	0.01	0.13	-4.35	🟦		🟪		Possible mixture of sources
Vail 1	11/20/2017	3.41	0.01	2.46	8.56	🟦		🟪		Possible mixture of sources
Van Meter 3	11/27/2017	1.01	0.01	3.68	5.50	🟦	🟫	🟪		Possible mixture of sources
Wall Lake 3	11/27/2017	29.37	0.01	1.15	6.29	🟦		🟪		Possible mixture of sources (known commercial fertilizer point source)
Waterloo 10	12/11/2018	0.26	0.01	7.73	5.49			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Waterloo 14	11/28/2017	10.02	0.01	1.41	-0.19	🟦		🟪		Possible mixture of sources (more likely to be commercial fertilizer)
Waterloo 17	11/28/2017	0.85	0.01	2.17	-5.43	🟦		🟪		Possible mixture of sources
Waterloo 18	12/11/2018	0.25	0.01	3.00	2.29	🟦	🟫	🟪		Possible mixture of sources
Waterloo 19	12/11/2018	0.55	0.01	9.70	6.04			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Waterloo 20	11/28/2017	4.22	0.01	1.25	-1.49	🟦		🟪		Possible mixture of sources
Waterloo 22	11/28/2017	5.99	0.01	6.28	-0.54		🟫	🟪		Possible mixture of sources
Waukon 2	11/27/2017	1.63	0.01	1.34	0.76	🟦		🟪		Possible mixture of sources
Waverly 5	3/19/2019	0.97	0.01	5.68	14.13		🟫	🟪		Possible mixture of sources
Waverly 6	3/19/2019	7.37	0.01	5.34	14.62		🟫	🟪		Possible mixture of sources
Waverly 6	11/20/2017	7.31	0.01	1.17	1.45	🟦		🟪		Possible mixture of sources
Waverly 7	3/19/2019	9.94	0.01	4.63	12.87	🟦	🟫	🟪		Possible mixture of sources
Waverly 7	9/28/2017	8.05	0.01	7.07	-0.38		🟫	🟪		Possible mixture of sources
Waverly 8	9/28/2017	8.94	0.01	-1.20	-9.01	🟦				Dominant source is most likely ammonia from commercial fertilizer (nitrate too high to be precipitation-derived)
Waverly 8	3/19/2019	8.10	0.01	5.33	15.39		🟫	🟪	🟩	Possible mixture of sources
Woodbine 1	12/11/2018	0.37	0.01	8.97	6.38			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Woodbine 2	12/11/2018	0.15	0.01	8.60	7.69			🟪		Dominant source is most likely ammonia in manure or septic waste, but denitrification may play a role
Woodbine 3	12/11/2018	0.03	0.01							Insufficient nitrate for isotopic analyses
Woodbine 4	12/11/2018	3.14	0.01	4.79	4.42	🟦	🟫	🟪		Possible mixture of sources