

Iowa DNR Ambient Groundwater Quality Monitoring Program Summary for FY18

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 important sources of drinking-water. Results of these analyses help us to understand which contaminants are present, how they are distributed, and whether their concentrations change over time. This report summarizes the results of the fiscal year 2018 (FY18) groundwater monitoring effort. Ambient groundwater monitoring data (2002 – 2017) are housed in the Iowa DNR's EQulS database and are available via the AQuIA website (<https://programs.iowadnr.gov/aquia/>) under "IowaGW."

The ambient groundwater quality monitoring effort in FY18 was designed to assess the occurrence of both natural and anthropogenic contaminants. Groundwater samples collected between October 2017 and March 2018 were analyzed for pH, total dissolved solids, nitrate+nitrite as N, ammonia as N, chloride, bromide, sulfate, iron, manganese, seven neonicotinoid insecticides, gross alpha and beta radioactivity, and five radionuclides from the uranium-238 decay series, including polonium-210 and lead-210. Wells that have contained nitrate in the past were analyzed for nitrogen and oxygen isotopes to help identify sources of nitrate.

Untreated water was collected from 118 municipal water supply wells across Iowa (Figure 1). These wells represented all major aquifer groups, and a wide range of depths, vulnerabilities based on estimated confining layer thicknesses, well ages, and types of land-use within the 2-year capture zone. An additional 16 wells were sampled only for isotopes of nitrogen and oxygen. These wells were selected by water operators that were interested in gathering information for source water protection planning. Samples were collected by certified water operators. IDNR staff collected duplicate samples at ten of the monitoring locations for quality control, along with two field blanks.

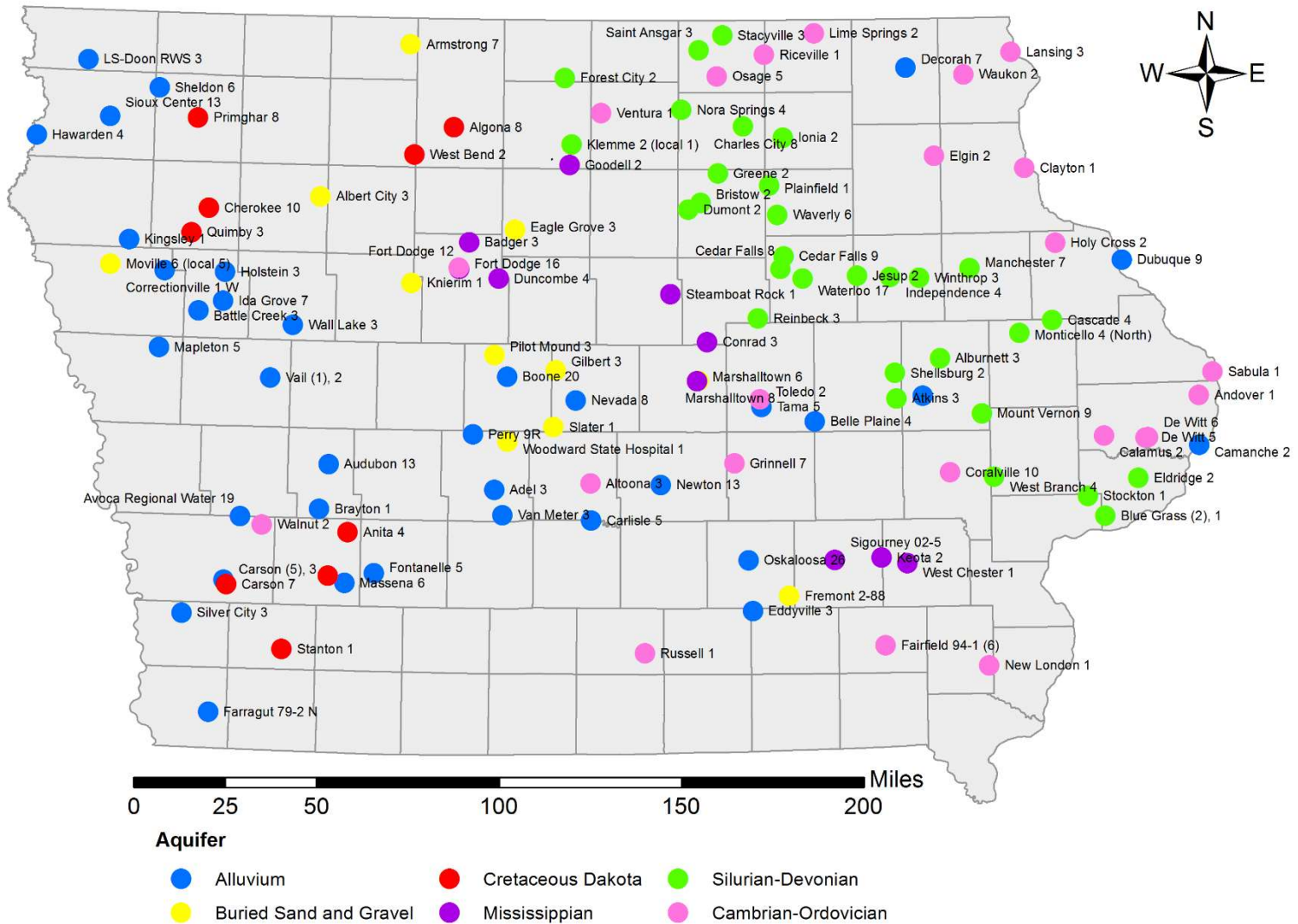


Figure 1. Locations of wells sampled in FY18 by aquifer group. This map does not include wells that were only sampled for nitrogen and oxygen isotopes.

New lessons from “old” analytes:

The water quality parameters listed in Table 1 have long been used to help us understand the treatment challenges posed by Iowa’s groundwater sources. These parameters can be used in new ways to help us assess the potential for contamination from natural or anthropogenic pollutants, and sometimes (like in the case of manganese) new information comes along which casts these compounds in a very different light.

Table 1. Summary of results for untreated groundwater samples taken from 118 wells in FY18. All analyses performed by the State Hygienic Laboratory.

Analyte	N	Det. limit(s) (mg/L)	Det. Freq. (%)	Mean of Detects (mg/L)	Min. (mg/L)	Median (mg/L)	75 th Percentile (mg/L)	Max. (mg/L)	Secondary Standard
pH	118			7.15	6.5	7.1	7.3	>10	6.5 – 8.5
Total Dissolved Solids	118	1.0	100	506	240	450	560	1950	500 mg/L
Chloride (Cl)	118	2 - 20	75	33.6	0.82	14.5	31.25	220	250 mg/L
Bromide (Br)	118	0.05	29	0.16	<0.05	<0.05	0.05	0.89	No standard
Sulfate (SO ₄)	118	1	96	99	<1	43	81	1100	250 mg/L
Iron (Fe)	54	0.02	59	0.05	<0.02	0.025	0.03	0.22	0.3 mg/L
Manganese (Mn)	54	0.02	48	0.18	<0.02	0.03	0.13	0.73	0.05 mg/L
Ammonia-nitrogen as N	118	0.05	63	1.16	<0.05	0.26	0.92	7	No standard
Nitrate + Nitrite as N	118	0.1, 0.2	36	6.6	<0.1	<0.1	3.1	29	MCL = 10 mg/L

Several of the parameters listed in Table 1 are known to have aesthetic, cosmetic, or technical effects on drinking-water supplies, and thus, have secondary drinking-water standards set by the U.S. EPA. Total dissolved solids (TDS), chloride, and sulfate, all contribute to salty tasting drinking-water. The majority of water samples obtained in FY18 fell below secondary drinking-water standards for these constituents. The Dakota sandstone aquifer in northwest Iowa is the “saltiest” with 55% of samples exceeding the TDS standard and 22% of samples exceeding the sulfate standard. Groundwater from deep Cambrian-Ordovician wells can also contain elevated TDS, with 48% samples over the secondary standard, and 24% of samples exceeding the secondary sulfate standard. TDS and sulfate generally increase to the southwest in Cambrian-Ordovician wells as these bedrock layers become deeper and the groundwater gets older, with more time to dissolve the rock (Figure 2).

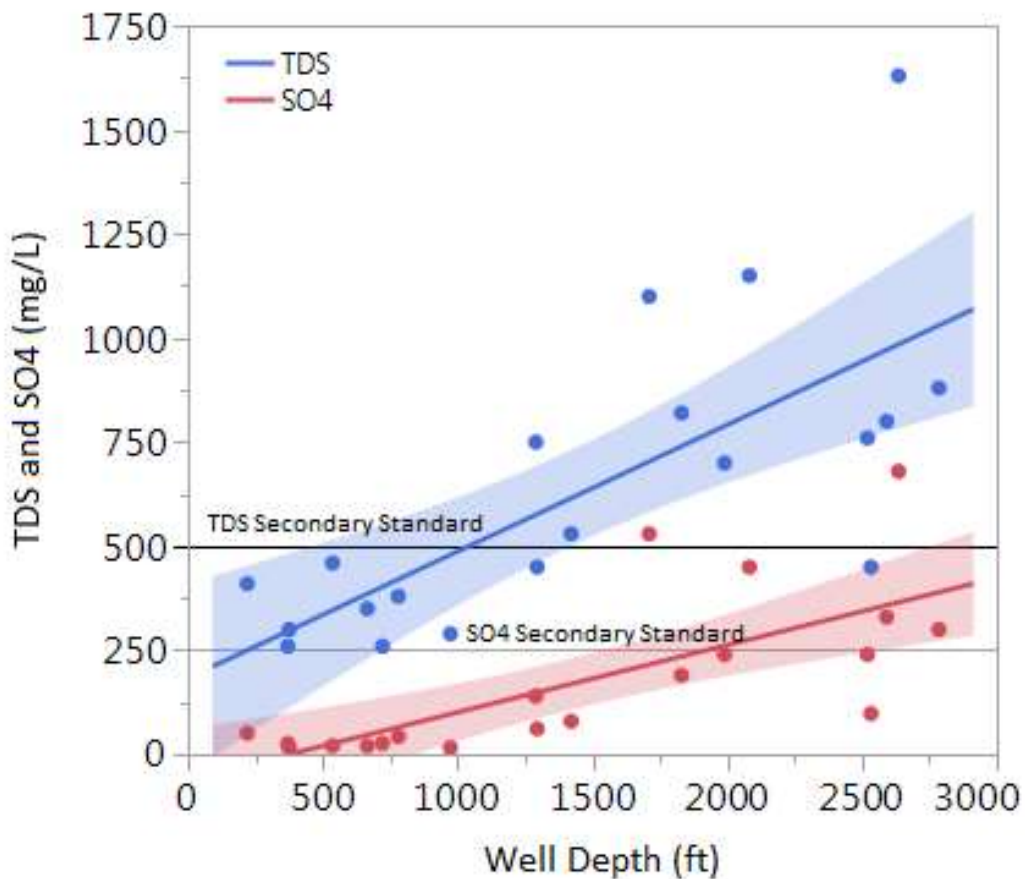


Figure 2. Concentrations of total dissolved solids (TDS) and sulfate (SO₄) in samples from Cambrian-Ordovician wells by well depth.

Groundwater content and ratios of various ions have been proposed as potential indicators of impacts on groundwater from waste treatment systems, agricultural activities, and use of road salt. In FY18, bromide was only found at concentrations above 0.2 mg/L in groundwater from Cambrian-Ordovician wells. As with other ions, bromide concentrations in Cambrian-Ordovician wells increased with depth.

Chloride/bromide ratios were significantly higher in samples with nitrate than those without ($p < 0.0001$). The median value of chloride/bromide ratios in samples without nitrate was 170 compared to samples with nitrate present where the median Cl/Br ratio was 760 (Figure 3). These results confirm that Cl/Br ratios could be used as a screening tool for groundwater contamination from surface activities. Further analysis would be necessary to determine whether these ratios could be used to help differentiate between sources of contamination.

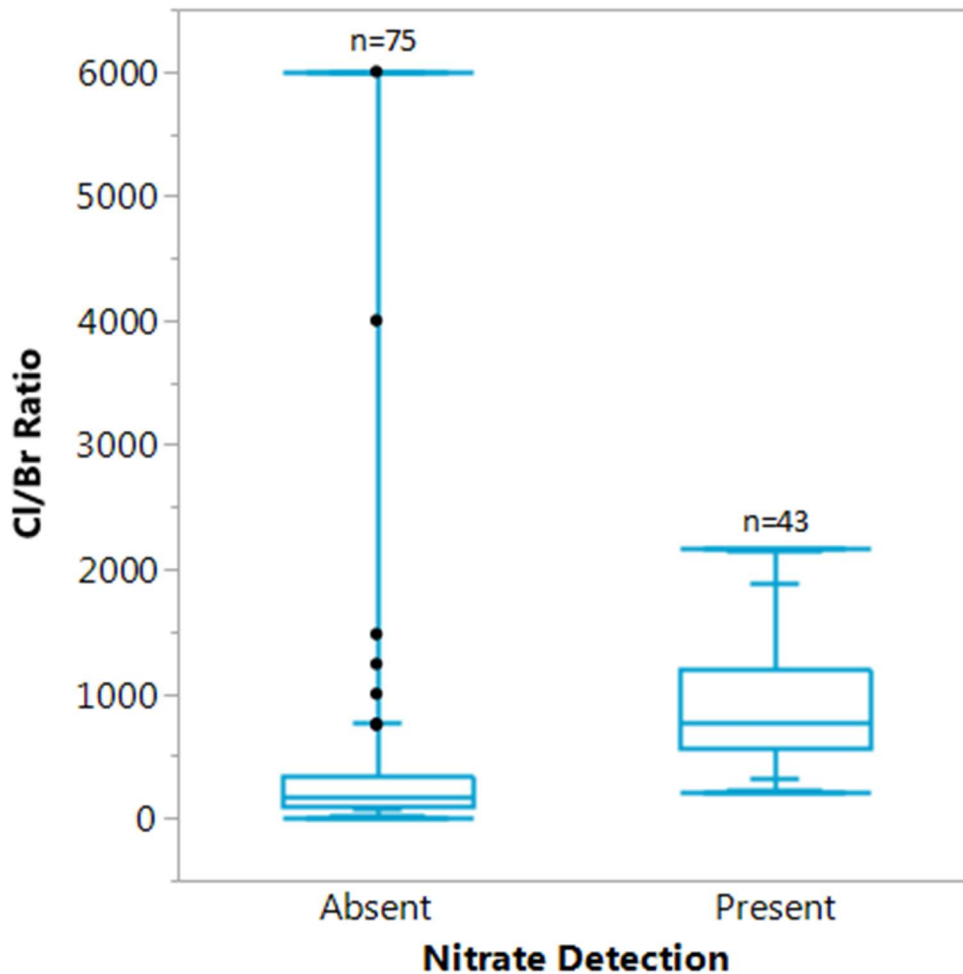


Figure 3. Quantile distributions of Cl/Br ratios in samples from FY18 with and without nitrate detections.

Manganese is a naturally-occurring element in groundwater that is known for causing aesthetic problems for drinking-water, such as black to brown color, staining, and bitter metallic taste, at levels greater than 0.05 mg/L. Recent studies have indicated that manganese may also have human health impacts. These studies have reported neurological effects, including decreases in memory and attention correlated to increased manganese concentrations in drinking-water, especially when concentrations exceed 0.1 mg/L (Bouchard et al., 2011; Oulhote et al., 2014). Infants are at greatest risk because their bodies are unable to excrete excess manganese (ATSDR, 2012). There is currently no primary drinking-water standard in the U.S. for manganese. Fortunately, many providers test their water and treat it to below 0.05 mg/L in order to avoid taste, odor, and staining complaints.

In FY18, samples from 54 wells were analyzed for manganese. These wells represented buried sand and gravel aquifers and bedrock aquifers, but did not include alluvial wells because these

were assessed for manganese in 2013. Manganese was detected in 48% of these wells, with 28% (15) of the wells above 0.1 mg/L. By combining this set of results with tests at other wells obtained since 2002, we can better understand the distribution of this element in Iowa's groundwater. What we see, is that the highest concentrations of manganese are found in alluvial aquifers. The highest concentrations of manganese generally occur in anoxic (low oxygen) groundwater with low nitrate concentrations. Many communities dependent on alluvial systems may have to balance the challenges posed by nitrate with the challenges posed by manganese and iron. Concentrations of manganese above 0.1 mg/L can also be found in groundwater (in order of descending average concentrations) from the Dakota aquifer, buried sand and gravel aquifers, the Mississippian bedrock aquifer, and the Silurian-Devonian aquifer system. Manganese has been detected in Cambrian-Ordovician wells, but only at very low concentrations.

Communities struggling with nitrate issues might consider using a deep confined aquifer as an alternative water source. Unfortunately, this often means trading one problem for another. Groundwater from deeper wells often contains nitrogen in the form of ammonia, which does not pose a direct risk to human health, but does interfere with chlorination at concentrations above 0.2 mg/L, and can also interfere with manganese removal systems. Of the 118 wells sampled in FY18, 103 (87%) contained detectable concentrations of nitrate or ammonia. Six wells (5%) contained detectable levels of both forms of nitrogen (all alluvial wells), and only 7 wells (6%) did not contain either form of nitrogen.

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 practices have contributed nitrate to their wells. In FY18, samples were collected from 60 wells for nitrogen and oxygen isotopic analyses which can be used to help differentiate between nitrate sources in groundwater (Kendall et al., 2007). Sampling locations included 44 wells that have been tested historically as part of the ambient groundwater monitoring network and 16 wells sampled by water operators interested in gaining additional information for their source water protection planning efforts. Samples from 5 wells did not contain sufficient nitrate to be processed for isotopes.

Ratios of ^{18}O to ^{16}O ($\delta^{18}\text{O}$) and ^{15}N to ^{14}N ($\delta^{15}\text{N}$) from nitrate were measured at the Nebraska Water Sciences Laboratory using an azide reduction and trace gas preconcentrator method. These ratios were then compared to standard values of mean ocean water and air, respectively, and reported in parts per thousand (‰). For both isotope pairs, a reported value of 1 is the equivalent to a measured ratio 1000 times higher than the standard. Based on analysis of duplicate field samples, $\delta^{18}\text{O}$ values vary less than 2.2 ‰, and $\delta^{15}\text{N}$ values vary less than 0.8 ‰.

Isotope results and corresponding nitrate concentrations are plotted in Figure 4. All of the FY18 groundwater samples fell in the -15 to 15 $\delta^{18}\text{O}$ ‰ range, indicating that the nitrate originated in the form of ammonia, either from commercial fertilizer, precipitation, soil ammonia, manure, or septic waste. Values of $\delta^{15}\text{N}$ above 7.5 ‰ suggest that the nitrate in these samples was most likely derived from manure or septic waste (20% of samples), while values of $\delta^{15}\text{N}$ below “0” suggest that the nitrate was derived from ammonia-based commercial fertilizer sources or ammonia in precipitation (15% of samples). Reported concentrations of ammonia in precipitation in Iowa rarely exceed 1 mg/L as N, therefore, it is unlikely that precipitation was the sole source of nitrate in all, but one, of these wells. Most (65%) samples contain $\delta^{15}\text{N}$ between 0 – 7.5 ‰, which means that the nitrate could be derived from multiple sources. For the 4 samples with relatively low concentrations of nitrate (<1 mg/L), and isotopic values between 2.5 – 7.5 ‰, it is possible that all of the nitrate was soil-derived.

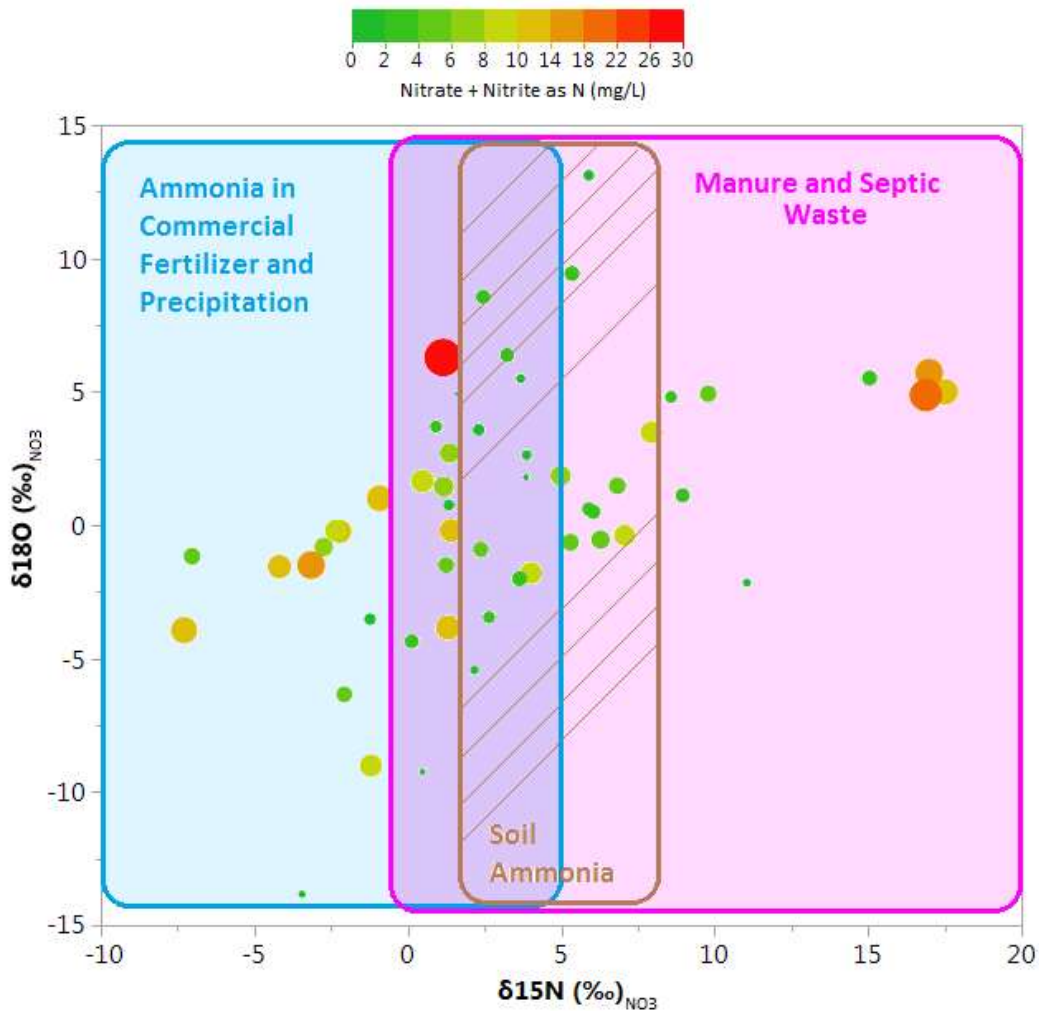


Figure 4. Nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) isotopic ratios for groundwater samples collected in FY18. Size and color of points correspond to reported concentration of nitrate + nitrite as N in the sample. Colored areas show the typical ranges of values for sources of groundwater nitrate published by Kendall et al., 2007.

It is important to consider 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 is present. In addition, the sources of nitrate may change seasonally, and from year to year, complicating the interpretation of these results. A thorough review of all available geological, hydrological, water quality, and well construction information is necessary before an effective plan to reduce nitrate concentrations can be formulated.

Occurrence of neonicotinoid insecticides in Iowa's groundwater:

In FY18, IDNR is partnering with researchers at the University of Iowa, who are working to understand the occurrence, exposure, and health consequences of the use of neonicotinoid insecticides in the environment. Estimates of neonicotinoid use in Iowa, and throughout the Midwest, have increased dramatically since 2004 (NAWQA, 2018). Neonicotinoids are used in both urban and rural environments to protect row-crops, orchards, ash trees, gardens, house plants, and pets, from insects.

Little is known about the health effects of these compounds on humans. The U.S. Environmental Protection Agency is currently reviewing the available research and developing risk assessments. There are currently no drinking water standards for these insecticides in the United States. These compounds have been shown to be highly soluble in water, increasing the risk of transport to surface and groundwater. Neonicotinoids have been detected in surface waters in the Midwest (Hladik et al., 2018). This sample collection is the first statewide assessment of neonicotinoids in Iowa's groundwater.

Samples from 118 wells were collected between October and March, and analyzed for seven neonicotinoid compounds: acetamiprid, clothianidin, dinotefuran, imidacloprid, sulfoxaflor, thiacloprid, and thiamethoxam. Results of this fall/winter sampling are summarized in Table 2. Thirty-seven percent of the wells had detections of one or more neonicotinoids: 19% contained a single neonicotinoid, 11% contained two neonicotinoids, 6% contained three compounds, and one sample (1%) contained a combination of four of these insecticides.

Table 2. Summary statistics for neonicotinoids in untreated water from 120 samples from municipal water supply wells collected in the fall/winter (2017-18) in Iowa. The detection limit for all samples was 0.096 ng/L. ND = not detected.

Neonicotinoid	Number of Detections	Detection Frequency (%)	Mean of Detections (ng/L)	Median of Detections (ng/L)	Quantiles of All Results		
					75% (ng/L)	90% (ng/L)	Max (ng/L)
Acetamiprid	0	0					
Clothianidin	41	34	2.91	0.98	0.22	3.22	12.79
Dinotefuran	1	1	1.32	1.32	ND	ND	1.32
Imidacloprid	15	13	0.49	0.22	ND	0.14	2.41
Sulfoxaflor	0	0					
Thiacloprid	0	0					
Thiamethoxam	18	15	2.23	0.41	ND	0.17	20.56

Neonicotinoids were detected more frequently in wells identified as highly vulnerable to contamination from the surface based on the estimated confining layer thickness. Neonicotinoids were present in 63% of wells completed in aquifers confined by less than 50 feet of low permeability materials, while only 14% of wells with thicker confining layers had positive detections.

Neonicotinoid insecticides are commonly applied in the spring and summer, and elevated concentrations have been observed in surface waters during the summer months (Hladik et al., 2018). In order to capture potential variability in those wells that are more likely to undergo seasonal variations, an additional round of sampling of the vulnerable subset of wells was completed between June – August, 2018 (results will be released at a later date).

Uranium-series radionuclides in groundwater:

Although much of the publicity regarding drinking-water quality in Iowa is focused on contamination caused by surface activities, naturally-derived contaminants associated with well-documented health effects also pose a serious challenge to public water supplies. While it is impossible to avoid exposure to radioactivity from natural sources, cumulative exposure to radioactivity increases the risk of developing cancer, therefore, it is important to understand and minimize potential exposures whenever possible. Although the gross alpha and gross beta standards are designed to assess the potential risk from multiple sources of radioactivity, knowing which radionuclides are present can greatly improve our understanding of overall risk. In FY18, water samples from 54 wells screened in buried sand and gravel or bedrock aquifers were analyzed for gross alpha radioactivity (including uranium), gross beta radioactivity, radium-226, uranium-234, uranium-238, polonium-210, and lead-210 by the State Hygienic Laboratory.

Table 3 summarizes the results of analyses for radioactivity for FY18 samples. Samples from 9 wells (17%) contained activities of Ra-226 above the combined radium standard of 5 pCi/L. Measured values greater than the minimum detectable activity (MDA) of Po-210 were reported for 41 of the 54 samples (76%). Seventeen samples (31%) had measured activities of lead-210 above the MDA. Lead-210 activities were significantly higher in samples from wells screened in the Dakota aquifer. While higher levels of Po-210 were also observed in samples from the Dakota, they were not statistically different from the other aquifers sampled in FY18. None of the samples contained Po-210 or lead-210 activities above the MDH’s estimated 1:10,000 cancer risk values.

Table 3. Summary of radionuclide analyses for FY18 groundwater sampling (N=54).

Radionuclide	Uncertainty Range (pCi/L)	MDA Range (pCi/L)	Summary statistics (pCi/L)			
			Min	Median	Mean	Max
Gross Alpha including Uranium	0.7 - 3.1	0.8 – 3.2	<MDA	3.55	5.28	28.8
Gross Beta	0.9 - 2.0	1.4 – 2.6	<MDA	5.3	6.58	33.7
Radium-226	0.1 - 0.6	0.5 – 0.9	<MDA	3.275	2.70	14.6
Uranium-234	0.026 - 0.403	0.012 – 0.236	0	0.397	0.716	3.0
Uranium-238	0.020 - 0.222	0.013 – 0.182	0	0.115	0.181	1.27
Polonium-210	0.0354 - 0.165	0.0123 – 0.120	0	0.159	0.134	0.597
Lead-210	0.07-0.376	0.245 – 0.440	-0.546*	0.169	0.201	0.977

*Negative values reported for lead-210 are the result of measured values minus background values.

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