FY2015 Ambient Groundwater Quality Monitoring Summary

lowa DNR's Ambient Groundwater Quality Monitoring program was suspended in 2006 due to the high costs of outsourcing the program. Since then, efforts to collect groundwater quality data have been sporadic. In 2012, reassessment of the program began. Lessons learned from the 2013 survey of emerging contaminants in lowa's groundwater¹, review of past data, and input from stakeholders, pointed towards a need to further assess groundwater contaminants that are not regularly monitored by public or private water supplies, such as herbicides and pharmaceuticals. In Iowa, occurrence of herbicides is significantly greater in wells with little or no protection from confining materials¹, and it is reasonable to expect pharmaceuticals originating from human waste and other sources near the ground surface are also more likely to occur in these wells. Thus, the primary objective of FY2015's ambient groundwater monitoring was to evaluate the occurrence and distribution of selected herbicide and pharmaceutical compounds in Iowa's vulnerable aquifers.

Fifty vulnerable municipal water supply wells were selected to be sampled in the Fall/Winter of 2014-2015. Forty-five municipal water operators submitted raw (untreated) groundwater samples, while the other five were unable to sample due to cold conditions and other operational limitations. Of the wells sampled, 30 tapped alluvial aquifers, 11 drew water from Silurian-Devonian aquifers, 1 from the Dakota aquifer, 1 from the Mississippian aquifer, and 2 from the Cambrian-Ordovician aquifer in northeastern lowa (Figure 1). All samples were analyzed by the State Hygienic Laboratory for basic water quality parameters, nutrients, atrazine and two of its breakdown products, chloroacetanilide herbicides and their ethanesulfonic acid (ESA) and oxanilic acid (OXA) degradates, and a suite of 16 pharmaceuticals.

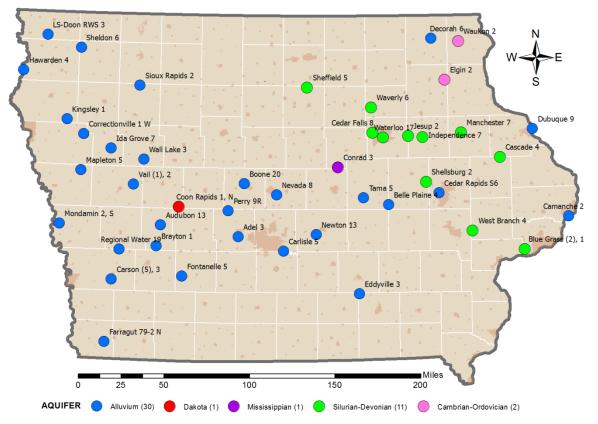


Figure 1. Locations of ambient groundwater samples for FY2015 colored by aquifer.

A basic summary of the results of nutrient, herbicide, and pharmaceutical analyses are presented in Table 1. All results will be entered into the Iowa DNR's EQuIS database and made available in GIS format via the Groundwater Quality geodatabase.

Group	Analyte	Limit of	N	Number of	Percent	Mean of	Median of	Maximum
	-	Detection		Detections	Detections	Detections	all values	
Nutrients	Nitrate + Nitrite nitrogen as N	0.1 mg/L	45	33	73	4.8	2	17
	Ammonia Nitrogen as N	0.05 mg/L	45	21	47	0.38	ND	1.60
	Total Kjeldahl Nitrogen as N	0.1 mg/L	45	19	42	0.4	ND	1.6
	Total Phosphorus as P	0.02 mg/L	45	45	100	0.14	0.10	0.81
	Ortho-Phosphate as P	0.02 mg/L	45	25	56	0.067	0.027	0.140
Herbicides and Degradates	Atrazine	0.020 μg/L	44	12	27	0.065	ND	0.240
	Desethyl Atrazine	0.020 μg/L	44	16	36	0.061	ND	0.200
	Desisopropyl Atrazine	0.020 μg/L	44	2	5	0.022	ND	0.023
	Acetochlor	0.025 μg/L	44	0	0	ND	ND	ND
	Acetochlor ESA	0.025 μg/L	44	24	55	0.211	0.030	0.770
	Acetochlor OXA	0.025 μg/L	44	13	30	0.271	ND	1.300
	Alachlor	0.025 μg/L	44	0	0	ND	ND	ND
	Alachlor ESA	0.025 μg/L	44	25	57	0.284	0.058	0.750
	Alachlor OXA	0.025 μg/L	44	8	18	0.395	ND	1.600
	Dimethenamid	0.025 μg/L	44	0	0	ND	ND	ND
	Dimethenamid ESA	0.025 μg/L	44	3	7	0.048	ND	0.057
	Dimethenamid OXA	0.025 μg/L	44	3	7	0.049	ND	0.092
	Metolachlor	0.025 μg/L	44	5	11	0.275	ND	0.600
	Metolachlor ESA	0.025 μg/L	44	38	86	0.483	0.310	1.900
	Metolachlor OXA	0.025 μg/L	44	21	48	0.247	ND	1.600
Pharmaceuticals	Acetaminophen	0.025 μg/L	45	0	0	ND	ND	ND
	Caffeine	0.025 µg/L	45	8	18	0.077	ND	0.200
	Carbamazepine	0.01 µg/L	45	0	0	ND	ND	ND
	Cotinine	0.01 µg/L	45	0	0	ND	ND	ND
	DEET	0.025 μg/L	45	0	0	ND	ND	ND
	Diclofenac	0.025 μg/L	45	0	0	ND	ND	ND
	Gemfibrozil	0.025 μg/L	45	1	2	0.057	ND	0.057
	Ibuprofen	0.010 μg/L	45	0	0	ND	ND	ND
	Lincomycin	0.010 µg/L	45	0	0	ND	ND	ND
	Metoprolol	0.010 μg/L	45	0	0	ND	ND	ND
	Sulfadimethoxine	0.010 μg/L	45	0	0	ND	ND	ND
	Sulfamethazine	0.010 μg/L	45	1	2	0.020	ND	0.020
	Sulfamethoxazole	0.010 μg/L	45	3	7	0.029	ND	0.036
	Sulfathiazole	0.010 μg/L	45	0	0	ND	ND	ND
	Triclosan	0.025 μg/L	45	0	0	ND	ND	ND
	Trimethoprim	0.025 μg/L	45	0	0	ND	ND	ND

Table 1. Summary of results for nutrients, herbicide compounds, and pharmaceuticals.Values below the limit of detection are denoted by ND.

Nitrate + nitrite as nitrogen (N) was detected in 73 percent of the vulnerable wells with a mean concentration of the detections at 4.8 mg/L, and a maximum concentration of 17 mg/L. Conversion of ammonia to nitrate only occurs when oxygen is present in soils, and denitrification often occurs in low-oxygen conditions. Thus, the lack of nitrate does not necessarily indicate a lack of nitrogen sources. In fact, all 12 samples that did not contain nitrate, contained detectable levels of ammonia nitrogen,

ranging from 0.07 – 1.6 mg/L as N. The highest nitrate concentrations were found in alluvial aquifers in western Iowa (Figure 2).

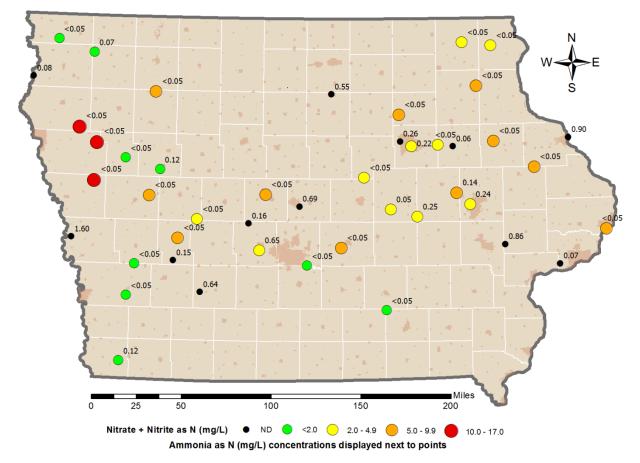


Figure 2. Nitrate + nitrite as nitrogen (N) concentrations in ambient groundwater samples from FY2015. Measured concentrations of ammonia nitrogen as N are shown next to the symbol.

In past years the reporting limit for atrazine for ambient groundwater samples was $0.1 \mu g/L$. Improvements to the method by SHL in 2014 lowered the detection limit to $0.02 \mu g/L$. While only one sample exceeded the pre-2014 reporting limit, 12 (27%) of the samples collected had detectable levels of atrazine at the lower detection limit. This improvement allows us to see the distribution of low levels of atrazine in vulnerable aquifers. Atrazine detections occurred more frequently in the eastern portion of the state, while samples from alluvial aquifers in western lowa showed no atrazine detections with the exception of the far northwest corner of the state (Figure 3).

The occurrence of pesticides (including herbicides) have been widely studied^{2,3}, but drinking-water standards have not been established for many of these compounds. All measured concentrations of atrazine and alachlor in FY2015 samples were below the maximum contaminant levels of 3 μ g/L and 2 μ g/L, respectively. For many other pesticide compounds, potential health risks from drinking-water exposures are a concern, but more data on health effects are needed to determine appropriate standards. Acetochlor and its ESA and OXA degradates, alachlor ESA and OXA, and metolachlor and its ESA and OXA degradates are listed on the Environmental Protection Agency's Contaminant Candidate List 3.⁴

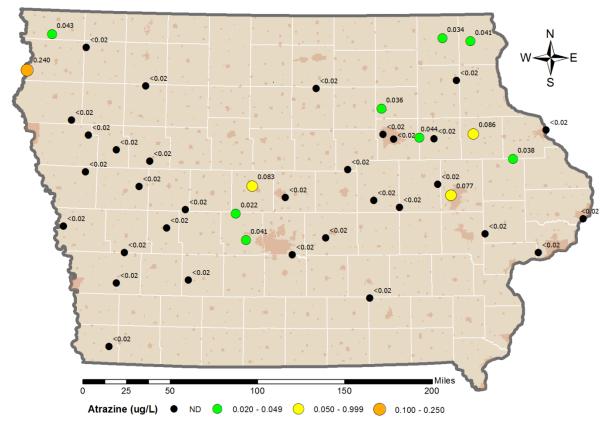


Figure 3. Map of atrazine results for FY2015. Numbers above locations indicate measured concentrations.

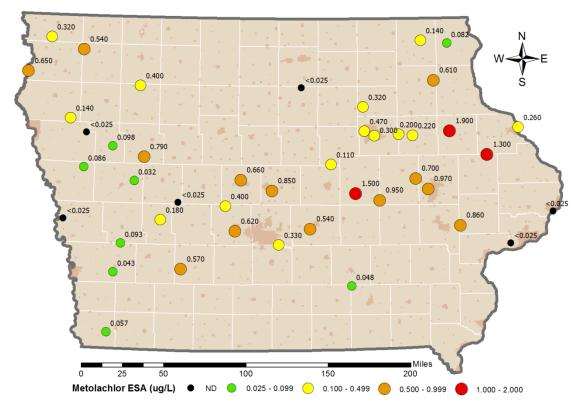


Figure 4. Map of metolachlor ESA results from FY2015. Numbers above locations indicate measured concentrations.

As with past groundwater studies in Iowa^{5,6,7}, results of FY2015 analyses showed that chloroacetanilide herbicide degradates were more prevalent than their parent compounds (metolachlor, alachlor, acetochlor, and dimethanamid). The most common herbicide compound was metolachlor ESA, with a maximum concentration of 1.9 μ g/L. Although more widespread than atrazine, the distribution of metolachlor ESA in groundwater is similar to atrazine, with the lowest concentrations generally occurring in western Iowa's alluvial aquifer systems (Figure 4). Mixtures of up to 12 different herbicides compounds were found in individual wells samples, with a maximum cumulative herbicide concentration of 5.090 μ g/L (Figure 5).

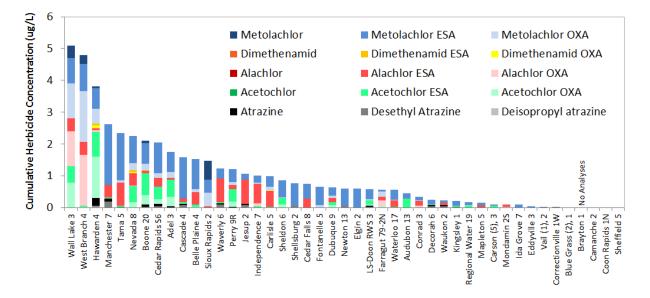


Figure 5. Mixtures of herbicide compounds by well.

The 2013 study of groundwater quality in 66 wells representing all of Iowa's major aquifers reported very low levels of one or more pharmaceuticals in 35% of wells using analytical methods developed by the USGS for 112 compounds.¹ Of the 14 pharmaceuticals detected in 2013, the most common was caffeine (25% of samples), followed by a breakdown product of caffeine. Similarly, caffeine was the most commonly detected pharmaceutical in FY2015 (18% of samples). Of the 16 pharmaceuticals analyzed in FY2015, only sulfamethoxazole, sulfamethazine, and gemfibrozil were detected in addition to caffeine. Sulfamethoxazole is an antibiotic used to treat infections in humans, and sulfamethazine is an antibiotic commonly used to treat livestock. Gemfibrozil is a drug used to treat high cholesterol.

Results presented for FY2015 represent groundwater that is highly vulnerable to contamination from surface activities due to a lack of protective confining material. These wells were not specifically selected to represent urban or rural land use, and analysis of the relationship between land use in the capture zones of these wells and contaminant concentrations has not yet been completed. All of the samples were collected during the late fall and winter in order to avoid short-term variations in concentrations driven by precipitation events or land application of chemicals. Concentrations reported here are thought to be baseline levels; however, more frequent monitoring would be necessary to determine whether these concentrations are sustained year-round, and the SWRL2 study of private wells showed higher percentages of detections during the dry (Oct – March) period than during the wet (April – Sept) season⁷. Further comparisons to herbicide data collected in previous years are planned.

Finally, it is very important to point out that concentrations of these contaminants in untreated water are not necessarily representative of the quality of water that reaches drinking-water users. Many communities that depend on vulnerable aquifers mix from multiple wells within the aquifer, or multiple aquifers, and some treatment methods are effective at removing organic compounds. Because private wells are less likely to be tested or treated for organic contaminants, efforts to assess and mitigate risks of organic contaminant exposures for private well users, like the 2008-2008 SWRL2 study⁷ and the Grants-to-Counties Program⁸, should be continued.

References

- 1 –Hruby, C.E., Libra, R.D., Fields, C.L., Kolpin, D.W., Hubbard, L.E., Borchardt, M.R., Spencer, S.K., Wichman, M.D., Hall, N., Schueller, M.D., Furlong, E.T., and P.J. Weyer, 2015. 2013 Survey of Iowa Groundwater and Evaluation of Public Well Vulnerability Classifications for Contaminants of Emerging Concern, Iowa Geological and Water Survey – Technical Information Series 57, 107 p.
- 2 Toccalino, P.T., Norman, J.E., and K.J. Hitt, 2010. Quality of Source Water from Public-Supply Wells in the United States, 1993-2007. National Water-Quality Assessment Program, Scientific Investigations Report 2010-5024, url: <u>http://pubs.usgs.gov/sir/2010/5024/pdf/sir20105024.pdf</u>, 126 p.
- 3 Kolpin, D.W., Barbash, J.E., and R.J. Gilliom, 2001. Major herbicides in ground water: results from the National Water-Quality Assessment, Journal of Environmental Quality, V. 28, n. 3, p. 103-112.
- 4 Environmental Protection Agency, 2009. Contaminant Candidate List 3, url: <u>http://www2.epa.gov/ccl/contaminant-candidate-list-3-ccl-3</u>, accessed August 24, 2015.
- 5 Kolpin, D.A., Hallberg, G.R., and Libra, R.D. 1997, Temporal Trends of Selected Agricultural Chemicals in Iowa's Groundwater, 1982-1995: Are things getting better?: Journal of Environmental Quality, v. 26, n. 4, p. 1007-1017.
- 6 Kolpin, D.W., Kalkhoff, S.J., Goolsby, D.A., Sneck-Fahrer, D.A., and Thurman, E.M. 1997, Occurrence of Selected Herbicides and Herbicide Degradation Products in Iowa's Ground Water, 1995: Ground Water, v. 35, n. 4, p. 679-688.
- 7 Center for Health Effects of Environmental Contamination, 2009. Iowa Statewide Rural Well Water Survey Phase 2 (SWRL2) Results and Analyses, report submitted to the Iowa Department of Natural Resources, url: <u>http://www.cheec.uiowa.edu/research/SWRL2%20results.pdf</u>, 27 p.
- 8 Iowa Department of Public Health, 2015. Grants to Counties Water Well Program website, url: <u>https://www.idph.state.ia.us/eh/grants.asp</u>.

By Claire Hruby, Ambient Groundwater Quality Monitoring Coordinator - IDNR