WATER RESOURCES DISCIPLINE
CENTRAL REGION
MINNESOTA WATER SCIENCE CENTER
Draft Proposal

A. TITLE

Assessing Arsenic Concentrations in Groundwater in Anoka County, Minnesota, 1992 - 2012

B. SUMMARY

Naturally occurring arsenic is common in groundwater in Minnesota. Drinking-water managers and producers need to know where high arsenic in groundwater is likely to occur before issuing well regulations, or permitting or investing in new production wells. Statewide arsenic results show that arsenic concentrations in Minnesota groundwater are higher in the western part of the state, but arsenic concentrations have significant spatial variability. In cooperation with the Minnesota Department of Health (MDH), the U.S. Geological Survey proposes to conduct a county-scale arsenic study in Anoka County, Minnesota.

Phase 2 of this study has three objectives: develop, implement, and evaluate a county-scale arsenic study for Anoka County, Minnesota, for the purpose of describing the two- and three-dimensional spatial distributions of arsenic in groundwater; test whether the probability of arsenic concentration exceedance is linked with one or more explanatory hydrogeologic, geochemical, and well-construction factors; and evaluate the adequacy of the county-scale arsenic study, including identifying outstanding data gaps and limitations.

The results of this study would contribute to the scientific understanding of arsenic in groundwater in Minnesota and could be applicable to other glaciated areas of the world. These results also would meet USGS strategic goals of understanding water resources for the Nation and meet the Minnesota Department of Health needs to protect the citizens of the State by ensuring citizens have safe water supplies.

C. PROBLEM

Naturally occurring arsenic is common in groundwater in Minnesota. Drinking-water managers and producers need to know where high arsenic in groundwater is likely to occur before issuing well regulations, or permitting or investing in new production wells. In cooperation with the Minnesota Department of Health (MDH), the U.S. Geological Survey proposes to assess two- and three-dimensional spatial distribution of high arsenic groundwater in Anoka County, Minnesota.

Arsenic is most likely to be present in glacial aquifers and shallow bedrock aquifers that lie within the area of the northwest provenance of Late Wisconsin-aged glaciations (Des Moines lobe). Erickson and Barnes (2005) found that high arsenic concentrations, defined as greater than the Maximum Contaminant Level of 10 micrograms per liter (μg/L) (USEPA, 2001), were more common in domestic wells and monitoring wells than in public-water supply wells. Arsenic also was prevalent in domestic wells where short well screens were set in proximity to confining units such as glacial till.

Because of concerns about human exposure to arsenic from drinking water, the Minnesota well code was updated by MDH in 2008 to require analysis for arsenic when drinking-water wells are installed. There are approximately 200 fully licensed well drillers in Minnesota, and there are approximately 20 private laboratories are certified to analyze arsenic in drinking water. Michael Convery, Well Management Section Operations Unit Supervisor, MDH, indicates that laboratories provide sample containers and instructions for sample collection to well drillers. Drillers collect the arsenic samples, and they may collect the sample either of raw water off the rig or finished water through the completed drinking water system (Convery, 2009).

The new arsenic testing rule could result in as many as 10,000 new analyses per year. Improved knowledge of the major factors influencing the occurrence and behavior of arsenic in glacial and bedrock aquifers, such as redox conditions, ammonia and iron concentrations, and shale contents of Des Moines Lobe deposits, could result in development of effective predictive tools for arsenic in groundwater. The number of required samples could potentially be decreased if some areas of the State are found to be at very low risk for arsenic contamination and could thus be excluded from the routine arsenic testing rule.

D. BACKGROUND

Past Statewide and West-central Minnesota Arsenic Studies

Two statewide groundwater quality assessments that measured arsenic were conducted in Minnesota during the 1990s (Centers for Disease Control, 1994; Minnesota Pollution Control Agency, 1995). Additionally, Minnesota's Public Water Systems (PWS) are located statewide and have measured arsenic concentrations. Statewide arsenic results show that arsenic concentrations in Minnesota groundwater are higher in the western part of the state, but arsenic concentrations have significant spatial variability. The Minnesota Arsenic Study (MARS) investigated arsenic occurrence and health effect biomarkers in western Minnesota during 1998-9 (Minnesota Department of Health, 2001). The MARS summary report hypothesized that high arsenic concentrations in groundwater are likely due to pyrite oxidation and an arsenic 'sweeping' mechanism involving pyrite cycling. Kanivetsky (2000) hypothesized that high-arsenic source material and arsenic adsorption/desorption mechanisms control arsenic concentrations in Minnesota groundwater.

In the upper Midwest, USA, Erickson (2005) found that high arsenic concentrations in groundwater were related to the presence of northwest provenance Late Wisconsinan glacial deposits. Wells screened in glacial deposits and shallow bedrock wells overlain by this glacial sediment are much more likely to have high arsenic groundwater. Evidence suggests that the distinct physical characteristics of the northwest provenance Late Wisconsinan glacial deposits cause the geochemical conditions necessary to mobilize arsenic. This fine-grained, comparatively organic-rich, biologically-active sediment creates a geochemical environment that is favorable to a regional-scale mobilization of arsenic in groundwater via reductive mobilization mechanisms such as reductive dissolution and reductive desorption. Arsenic concentrations were positively correlated to analytes like iron and manganese, negatively correlated to analytes like chloride and bromide, and not correlated to carbonate, sulfate, total organic carbon, or ammonium. There was a weak negative correlation between phosphorous and arsenic. Arsenic present in groundwater was aqueous, and most of the arsenic present in Minnesota groundwater was As(III).

Kanivetsky (2000) summarized the arsenic concentrations measured in Minnesota Quaternary sediments. Mean arsenic concentrations range from <0.1 mg/kg to 26 mg/kg in the western part of the state, which is higher than concentrations measured in sediments in the eastern part of the state, where they range up to 11 mg/kg. Although categorized as 'eastern' and 'western,' all of the sample locations are within the footprint of Late Wisconsinan glacial sediments of northwestern source provenance.

Additionally, arsenic contamination was more common in domestic wells and monitoring wells than in public water system wells, and arsenic contamination was more prevalent in domestic wells with a short screen set in proximity to an upper confining unit, such as till. The geochemical environment at the interface between the confining unit and the aquifer (McMahon, 2001) is conducive to arsenic mobilization. Public water system wells have distinctly different well construction practices and well characteristics when compared to domestic and monitoring wells. Public water system well construction practices such as seeking a thick, coarse aquifer and installing a long well screen, which are more likely to yield good water quantity. These well construction practices also, coincidentally, often yield low arsenic.

2010-2011 USGS Study of Arsenic Concentrations in Carlton, Anoka, and Otter Tail Counties

MDH provided USGS with the following data sets for this study:

- County Well Index for Anoka, Carlton, and Ottertail Counties, provided in June 2010, and an update for Anoka County provided in March 2011
- Historic arsenic data from MPCA's GWMAP project, Public Water System raw water, and MDH arsenic study for Anoka, Carlton, and Ottertail Counties, provided in September 2010
- New arsenic data from new domestic wells drilled in Anoka, Carlton, and Ottertail counties, provided in July 2010

USGS obtained the following data sets for the study:

- Carlton County Atlas – Part A
- RHA 1 – Anoka Sand Plain
- RHA 3 – Southern Red River Valley
- RHA 5 – Otter Tail
- 'Extra' arsenic data: Preliminary trace element data from DNR, Carlton County Atlas Part B

Wells that had both an arsenic concentration and an adequately detailed record in CWI were included in the descriptions of arsenic concentrations, geologic setting, and well construction characteristics. Approximately half of the arsenic concentrations provided to USGS by MDH were not able to be used in the study because of incomplete or missing CWI well records.

Anoka County

A total of 58 historic and 269 new well arsenic measurements (327 total) were provided with complete CWI well records. Because of missing CWI records, 34 arsenic measurements were omitted from the analysis for Anoka County. Figure 1 illustrates the areal distribution of measured well water arsenic concentrations. A total of 10.7% of wells had arsenic concentrations exceeding 10 µg/L. Concentrations ranged from not detected to 41.38 µg/L in Anoka County.

Tables 1 and 2 provide elevated arsenic concentration frequencies by aquifer and well depth. Although no clear geologic indicator for elevated arsenic was identifiable from this study using only existing data, two general observations are notable. Wells with screens within a buried quaternary or open to the Franconia, Ironton, and/or Galesville (F-I-G-) formations had a higher likelihood of elevated arsenic concentration. Additionally, on average, shallower F-I-G bedrock and deeper quaternary wells more likely to have elevated arsenic.

Carlton County

A total of 15 historic and 20 new well arsenic measurements (35 total) were provided with complete CWI well records. Because of missing CWI records, 145 arsenic measurements were omitted from the analysis for Carlton County. USGS was also able to obtain arsenic concentrations for 89 wells sampled by DNR as part of its Part B County Geologic Atlas work for Carlton County. Therefore, a total of 124 wells were included in the study. Figure 2 illustrates the areal distribution of measured well water arsenic concentrations. A total of 5.6% of wells had arsenic concentrations exceeding 10 µg/L. Concentrations ranged from not detected to 20.4 µg/L in Carlton County.

Tables 3 and 4 provide elevated arsenic concentration frequencies by aquifer, proximity of well screen or open interval to upper confining unit (clay gap), and well depth. Although no clear geologic indicator for elevated arsenic was identifiable from this study using only existing data, two general observations are notable. Wells with screens within a buried quaternary or open to the Thompson or Fond Du Lac formations had a higher likelihood of elevated arsenic concentration. Additionally, on average, well screens or open intervals in proximity to the upper confining unit were more likely to have elevated arsenic. The number of wells in this study is relatively small.

Otter Tail County

A total of 364 historic and 77 new well arsenic measurements (441 total) were provided with complete CWI well records. Many additional incomplete well records (lacking well construction or geologic information) were also provided. Because of missing CWI records, 477 arsenic measurements were omitted from the analysis for Otter Tail County. Figure 3 illustrates the areal distribution of measured well water arsenic concentrations. A total of 45% of wells had arsenic concentrations exceeding 10 µg/L. Concentrations ranged from not detected to 162 µg/L in Otter Tail County. On average, deeper wells were more likely to have elevated arsenic concentrations than shallower wells. The well construction and geologic information provided in CWI for most Otter Tail County wells with arsenic concentration measurements was not sufficient to conduct more detailed three-dimensional analyses of results.

Also of note: only 20% of the arsenic measurements not included in the analysis due to missing well records exceeded 10 µg/L arsenic – significantly lower than the average for the wells included in the study.

Summary

Existing well-water arsenic concentrations, geologic information, and well construction information are adequate to broadly and generally summarize arsenic occurrence in Anoka, Carlton, and Otter Tail Counties. Existing data are not sufficient, however, to begin development of detailed, three-dimensional probability maps for elevated arsenic, predictive tools for elevated arsenic, or guidance for drilling low-arsenic wells.

E. OBJECTIVES AND SCOPE

The overall study objective is to better delineate and help explain groundwater arsenic concentrations in space and time. Phase 2 of the study has three specific objectives:

- Develop, implement, and evaluate a county-scale arsenic study for Anoka County, Minnesota, for the purpose of describing the two- and three-dimensional spatial distributions of arsenic in groundwater
- Test whether the probability of arsenic concentration exceedance is linked with one or more explanatory hydrogeologic, geochemical, and well-construction factors.
- Evaluate the adequacy of the county-scale arsenic study, including identifying outstanding data gaps and limitations.

F. RELEVANCE AND BENEFITS

The results of this study would contribute to the scientific understanding of arsenic in groundwater in Minnesota and could be applicable to other glaciated areas of the world. These results also would meet USGS strategic goals of understanding water resources for the Nation and meet the Minnesota Department of Health needs to protect the citizens of the State by ensuring citizens have safe drinking water supplies.

This project is relevant to the USGS strategic science vision (USGS, 2007), specifically in the areas of identifying environmental risk to the public and securing freshwater for America’s future. It is also relevant to the Water Resources Discipline priority issue of addressing the effects of urbanization and suburbanization of water resources (USGS, 1999).

G. APPROACH

The project will be completed collaboratively, with MDH and USGS each having specific and significant roles and work responsibilities.

The first major project task will be selecting approximately 400 target wells for geochemical sampling. This number was chosen to provide statistical strength to the analysis of results for several aquifers that are yet to be identified, and the target number of wells may be decreased if few aquifers are chosen as targets for sampling. MDH will complete this task with input from USGS. MDH will compile the following data sets:

- Up-to-date version of CWI for Anoka County, including ‘clay gap’ calculation and assignment of hydro-stratigraphic identifier for aquifers
- Up-to-date new-well arsenic data set for Anoka County
- Up-to-date PWS arsenic data for wells sampled in 2011
- List of PWS in Anoka County to be visited in 2012

MDH, with input from USGS, will develop an automated well-selection method to identify approximately 500 target wells, which will be geographically and stratigraphically balanced, for sampling during 2012. Of the 500 target wells, approximately 400 wells will actually be sampled. MDH should complete this task by December 2011.

After the initial selection of 500 wells, MDH will work iteratively using input from USGS, as needed, to ensure that the distribution of selected target wells meets the project needs for adequate three-dimensional spatial distribution of wells throughout the Anoka County. MDH and USGS should select final well target wells by March 2012.

By March 2012 or before beginning well sampling, MDH will provide the following information to USGS:

- QA/QC for MDH laboratory analytical methods to be used on collected groundwater samples
    - Written protocols/methods
    - Long-term results for accuracy, detection levels, etc.
- Groundwater sample collection protocols

MDH will contact well owners and collect the following raw-water (no treatment, such as softening, reverse osmosis, or other treatment) samples for analysis by an appropriate method in the field or at the MDH laboratory:

- At 400 (of the 500) wells chosen by MDH in consultation with USGS and Anoka County: field parameters, arsenic, dissolved O_2, NO_3^- (as Nitrogen), Mn^{2+}, Fe^{2+}, SO_4^{2-}, Sulfide (sum of H_2S, HS^-, S_2^-). Samples for dissolved nitrate, metals, and sulfur compound constituents may require field-filtering samples.
- At the first 20 of the wells above, collect replicate unfiltered samples to see whether filtered/unfiltered constituent concentrations are statistically the same. These results should be provided to USGS as they are obtained. If filtered and unfiltered results are statistically the same, then field-filtering samples may be dropped for the remainder of the samples.
- At 40 of the wells above, collect replicate samples. These results should be provided to USGS as they are obtained.
- At 10 of the above wells, collect field blanks for all laboratory methods. These results should be provided to USGS as they are obtained.

MDH may opt to provide grant funding to Anoka County for contacting well owners and collecting groundwater samples.

USGS will coordinate with MDH to conduct the following as part of the groundwater sampling effort during the 2012 field season:

- From approximately 20 wells sampled by MDH, collect arsenic and trace metal replicate samples and analyze at the USGS NWQL early in the sampling schedule.
- Provide sample bottles to MDH samplers for up to 4 trace metal field blanks early in the sampling schedule, analyze at USGS NWQL, targeting a minimum of one field blank for each MDH/Anoka County sampler.
- Collect and analyze approximately 40 samples for arsenic speciation analysis at USGS NWQL.

All groundwater sampling should be completed by MDH and USGS by October 2012.

After completing the groundwater sampling and laboratory analysis, MDH will compile all field parameter and laboratory analytical results collected by MDH/Anoka County in an electronic form that that may be linked with the Anoka County CWI. In addition, MDH will update the 'new well' arsenic data and the Anoka County CWI, and will compile the relevant analytical parameters (field parameters, arsenic, dissolved O_2, NO_3^- (as Nitrogen), Mn^{2+}, Fe^{2+}, SO_4^{2-}, Sulfide (sum of H_2S, HS^-, S_2^-)) from the 2012 PWS sampling effort. MDH will provide the compiled results to USGS. The updated Anoka County CWI augmented with the 'clay gap' calculation and hydro-stratigraphic unit assignment, compiled arsenic results used in well selection, the updated 'new well' arsenic data (for results received by MDH by October 2012), and 2012 field parameter and analytical data should be provided to USGS by December 2012.

After receiving the results of the 2012 groundwater arsenic sampling, USGS will conduct detailed two- and three-dimensional analysis of results to determine whether geologic, geochemical, hydrogeologic, well-construction characteristics, or other factors are related to the probability of elevated arsenic in well water.

Data will be analyzed using contingency table analysis (of arsenic classified into two or more concentration ranges) versus well characteristics (for example, depth of well screen below confining layer) or other factors. The contingency table analysis will be used to identify if there are significant differences in the likelihood of high arsenic in wells with different characteristics within the county. There will be no analysis of error or bias potentially introduced due to variability in sampling protocols and laboratory methods.

The results of the contingency table analysis will provide information to guide additional analysis of arsenic concentration ranges and geologic data. Further analysis will include looking for significant differences between wells of different depths but having other factors in common. For example, one possible finding would be that buried glacial aquifer wells located within the area of a particular geologic unit in the county are more likely to have high arsenic than wells in unconfined aquifers in the county. The buried glacial aquifer wells could be further divided into depth ranges, to see if there are significant differences between similar wells of different depths.

The wells sampled during 2012 will also be analyzed using non-parametric statistics to look for correlations between arsenic and water chemistry parameters. Results for new wells sampled prior to 2012 by a well driller that are resampled as part of the 2012 sampling effort will be analyzed to see if the results are statistically the same. A subset of wells in proximity with one another but with significantly differing arsenic concentrations will be analyzed in more detail. Factors that will be examined as possible contributors to differing arsenic concentrations are well construction materials, small zones of geologic material of differing hydraulic conductivity, well drilling method, well construction characteristics, and groundwater chemistry.

Using the methods of Jurgens and others (2009), a redox regime analysis will be conducted for all sample events with sufficient geochemical data. Arsenic is a redox-sensitive element. Applying this relatively new tool to Anoka County geochemical parameters may provide additional categorization – an indicator – of the likelihood of elevated arsenic in a particular well by identifying areas or zones where more reducing or more oxidizing conditions exist. The results of the arsenic speciation analytical results will also be used in the redox regime analysis.

The QA/QC samples (replicate samples, field blanks, and filtered/unfiltered sample pairs) will be used to conduct a complete analysis of data quality. Any identified data quality concerns will be discussed and data used in the rest of the analyses qualified, as appropriate.

Data analysis should be completed by USGS by September 2013.

Project results will be reported in a USGS Scientific Investigation series report and/or journal article. In addition to presentation of the technical results, a discussion of outstanding data gaps and limitations to the approached used for county-scale arsenic study will be presented. The report or journal article should be complete by December 2013.

H. PRODUCTS

The Phase 2 project products will be a USGS Scientific Investigation series report and/or a journal article.

I. WORK PLAN

The major work tasks are expected to be completed as illustrated in the following table. The indicated fiscal year is the Federal fiscal year.

Workplan Element	FY-2012				FY-2013				FY-2014			
Develop well selection scheme – MDH with USGS input	X											
Select 500 target wells - MDH		X										
Sample 400 of 500 target wells - MDH			X	X								
Sample subset of target wells - USGS			X	X								
Compile all geologic and geochemical data - MDH					X							
QA/QC analysis - USGS			X	X	X	X						
Redox regime analysis – USGS						X	X					
Statistical data analysis – USGS						X	X	X				
Write report/journal article – USGS								X	X			

J. FUNDING.

	FY- 2012	FY- 2013	FY- 2014	FY- 2015	FY- 2016
Funding Source	(all values in gross dollars)				
MN Dept. of Health	$26,078	$85,398	$10,733		
USGS	$7,392	$36,599	$4,600		
Totals	$33,470	$121,997	$15,333		

The funding included in the table is for Phase 2 work only.

K. BUDGET

The budget for Phase 2 work includes the following: Hydrologists, $133,000; Field Technician, $3,500; Database and GIS technician, $25,000; and Analytical and shipping, $8,800. USGS will provide a 30% match on project personnel costs.

L. PERSONNEL.

The following personnel will work on Phase 2 of the project.

Hydrologist GS 12/13 will provide overall project management, conduct two- and three-dimensional spatial statistical analysis, identify remaining data gaps, and write the SIR or journal article (approximately 7 months of time).

Database and GIS technician GS 7/8 will provide database and GIS support and prepare figures illustrating findings (approximately 2 months of time).

Hydrologic technician GS 6/7 will provide groundwater sampling support (approximately 2 weeks of time).

MDH will compile and provide to USGS electronic water quality, stratigraphic, and well construction information.

M. SAFETY.

No unusual safety hazards are expected as part of this project.

N. REFERENCES

Convery, M., 2009, Minnesota Department of Health, p. Communication with drillers regarding arsenic sampling.

Erickson, M.L., 2005, Arsenic in Upper Midwest Ground Water: Occurrence and Geochemical Mobilization Mechanisms, Ph.D Dissertation: Minneapolis, Minnesota, University of Minnesota.

Jurgens, B.C., McMahon, P.B., Chapelle, F.H., and Eberts, S.M., 2009, An Excel® Workbook for Identifying Redox Processes in Ground Water: US Geological Survey Open File Report 2009-1004, 8 p.

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USGS, 2007, Facing Tomorrow's Challenges— U.S. Geological Survey Science in the Decade 2007–2017: USGS Circular 1309, 81 p.

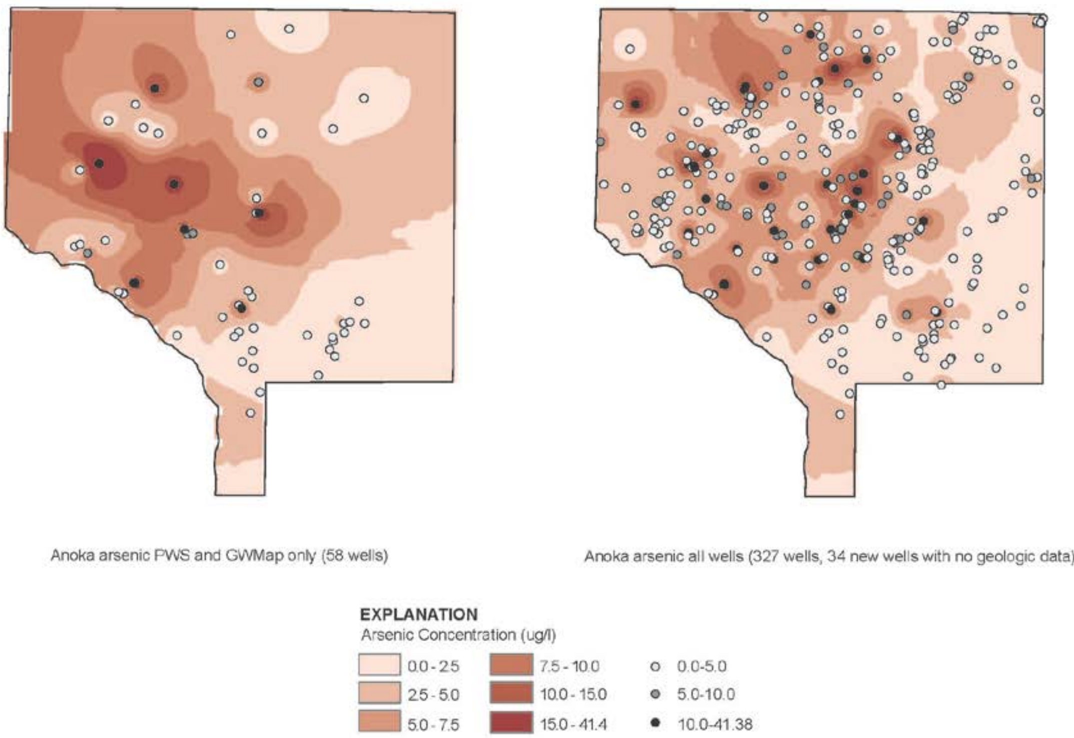

Figure 1 – Arsenic concentrations in well water, Anoka County, Minnesota

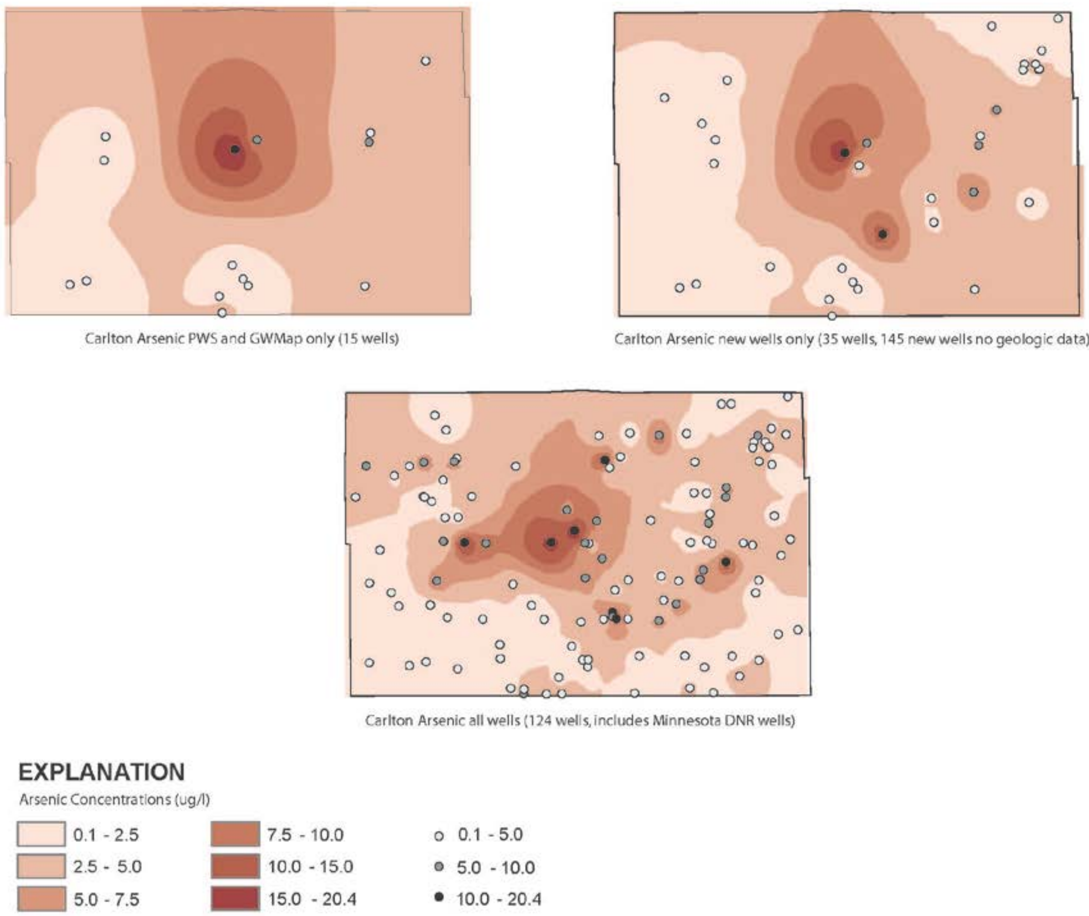

Figure 2 – Arsenic concentrations in well water, Carlton County, Minnesota

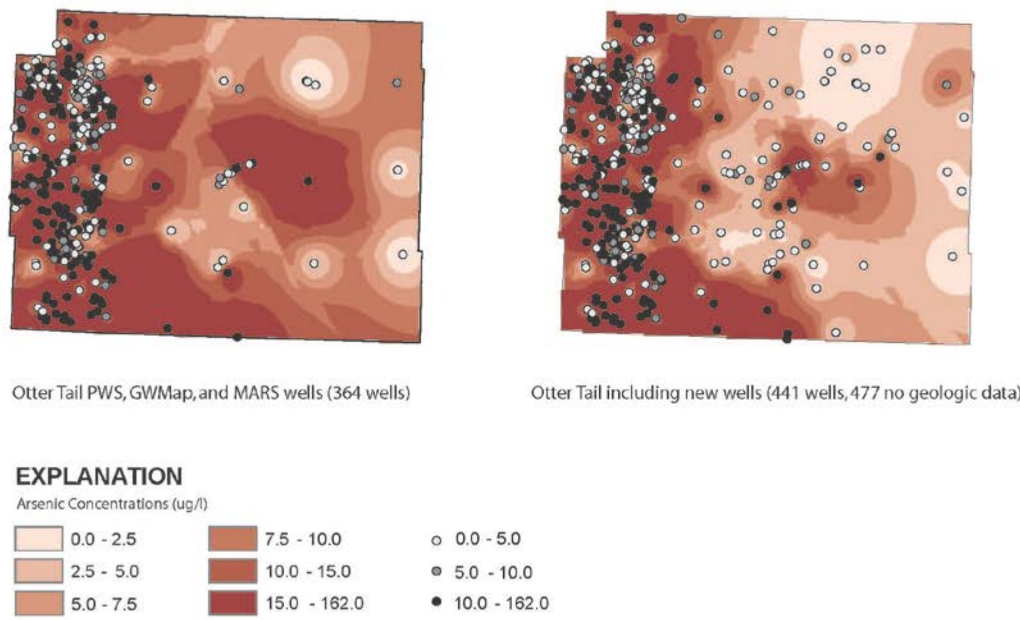

Figure 3 – Arsenic concentrations in well water, Otter Tail County, Minnesota

Table 1. Anoka County well water arsenic concentrations, counts above and below 10 ug/L, by aquifer

Aquifer	As≥10 ug/L	As<10 ug/L	Total	% As≥10
All	35	292	327	10.7%
QBAA - Quaternary Buried Artesian Aquifer	18	172	190	9.5%
QWTA - Quaternary Water Table Aquifer	0	12	12	0.0%
CSLF - St. Lawrence-Franconia	2	13	15	13.3%
CFRN - Franconia	6	57	63	9.5%
CSTL - St. Lawrence	0	6	6	0.0%
CJDN - Jordon	1	2	3	33.3%
CIGL - Ironton-Galesville	1	3	4	25.0%
CFIE - Franconia-Eau Claire	2	4	6	33.3%
CFIG - Franconia-Ironton-Galesville	2	5	7	28.6%
INDT - Indeterminate	3	0	3	100.0%
Wells Not Included	2	32	34	5.9%

Table 2. Anoka County well water arsenic concentrations, by aquifer and well depth

[N/A: Not Applicable]

Aquifer	% As ≥ 10 ug/L	Average Casing Depth (feet)	
		As≥10 ug/L	As<10 ug/L
All	10.7%	140	139
QBAA - Quaternary Buried Artesian Aquifer	9.5%	130	113
QWTA - Quaternary Water Table Aquifer	0.0%	N/A	78
CSLF - St. Lawrence-Franconia	13.3%	119	158
CFRN - Franconia	9.5%	127	165
CSTL - St. Lawrence	0.0%	N/A	133
CJDN - Jordon	33.3%	91	189
CIGL - Ironton-Galesville	25.0%	243	248
CFIE - Franconia-Eau Claire	33.3%	233	292
CFIG - Franconia-Ironton-Galesville	28.6%	182	235
INDT - Indeterminate	100.0%	Unknown	N/A

Table 3. Carlton County well water arsenic concentrations, counts above and below 10 ug/L, by aquifer and clay gap distance

Aquifer	As≥10 ug/L	As<10 ug/L	Total	% As≥10
All	7	117	124	5.6%
PETM - Thompson Formation				
Clay gap[1] ≤ 6'	2	15	17	11.8%
Clay gap > 6'	0	2	2	0.0%
PMFL - Fond du Lac Formation				
Clay gap ≤ 6'	1	4	5	20.0%
Clay gap > 6'	0	8	8	0.0%
QBAA - Quaternary Buried Artesian Aquifer				
Clay gap ≤ 6'	4	38	42	9.5%
Clay gap > 6'	0	22	22	0.0%
Wells not included	12	133	145	8.3%

[1]Distance from the bottom of the well casing to the bottom of the above confining unit

Table 4. Carlton County well water arsenic concentrations above and below 10 ug/L, by aquifer and well depth

[N/A: Not Applicable]

Aquifer	% As ≥ 10 ug/L	Average Casing Depth (feet)	
		As≥10 ug/L	As<10 ug/L
All	5.6%	114	117
PETM - Thompson Formation			
Clay gap ≤ 6'	11.8%	36	80
Clay gap > 6'	0.0%	N/A	91
PMFL - Fond du Lac Formation			
Clay gap ≤ 6'	20.0%	320	284
Clay gap > 6'	0.0%	N/A	359
QBAA - Quaternary Buried Artesian Aquifer			
Clay gap ≤ 6'	9.5%	82	95
Clay gap > 6'	0.0%	N/A	101

[1]Distance from the bottom of the well casing to the bottom of the above confining unit