Preliminary Assessment of Naturally-Occurring Manganese in Minnesota Groundwater

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Abstract

Interest in naturally-occurring manganese as a chemical component of groundwater and drinking water is increasing. The United States Environmental Protection Agency (USEPA) National Secondary Drinking Water Regulations (NSDWR) standard for manganese is 50 ug/L, and the Minnesota Department of Health (MDH) Health Risk Limit (HRL) is 100 ug/L. Because of concerns related to source water used in infant formula, MDH may soon apply these drinking water quality standards more widely than in the past. The MDH Source Water Protection (SWP) program prepared a summary of the natural distribution of manganese in Minnesota groundwater, using data from various federal, state, and county sources.

The statewide distribution of 4339 data points (Figure 1) had a log-normal frequency distribution, a median of 93 ug/L, and was strongly spatially correlated. The highest concentrations occurred in southwestern Minnesota and the lowest in southeastern Minnesota. Quaternary water table and buried artesian aquifer settings had the greatest median concentrations (155 and 160 ug/L, respectively), and the Paleozoic bedrock aquifers had the least (32 ug/L). Concentrations at 2123 wells (48.9%) exceeded the HRL. Buried artesian aquifer settings had the greatest percentage of wells exceeding the HRL (63.0%) and the Paleozoic bedrock aquifer had the least (24.3%).

Median concentrations in plastic-cased wells were twice those in metal-cased wells, suggesting that casing material may affect concentration. Hydrogeologic setting and factors related to well construction may also influence concentration. Several sampling efforts including manganese are in the planning stages or underway, ensuring that the manganese dataset continues to grow.

Background

Geochemical properties of manganese and iron are often considered together, though there are important differences (Hem, 2005). Manganese is much less abundant than iron in the earth's crust, but still widely distributed in rocks and soil. Manganese is much slower to precipitate than iron. Groundwater containing more manganese than iron is uncommon.Manganese commonly occurs in the Mn^{+2} (reduced) form, less commonly as Mn^{+4} (the Mn^{+3} ion is uncommon in water). These manganese ions strongly adsorb to metallic cations, forming coatings on mineral surfaces.

Description of Manganese in Groundwater

The data (Table 1) define a skewed, log-normal frequency distribution, with concentrations ranging from below detection to 5,040 ug/L. Water table and buried artesian aquifer settings have the greatest median manganese concentrations, and the Paleozoic bedrock aquifers have the least.

Manganese concentrations at 2,667 wells (Table 2) exceeded the MCL, and samples at 2,123 wells exceeded the HRL. Buried artesian aquifer settings had the greatest percentage of wells exceeding the HRL (63.0%) and the Paleozoic bedrock aquifer had the least (24.3%). Figures 2 and 3 show the spatial distribution of available manganese data for Quaternary buried artesian and Paleozoic bedrock aquifers.

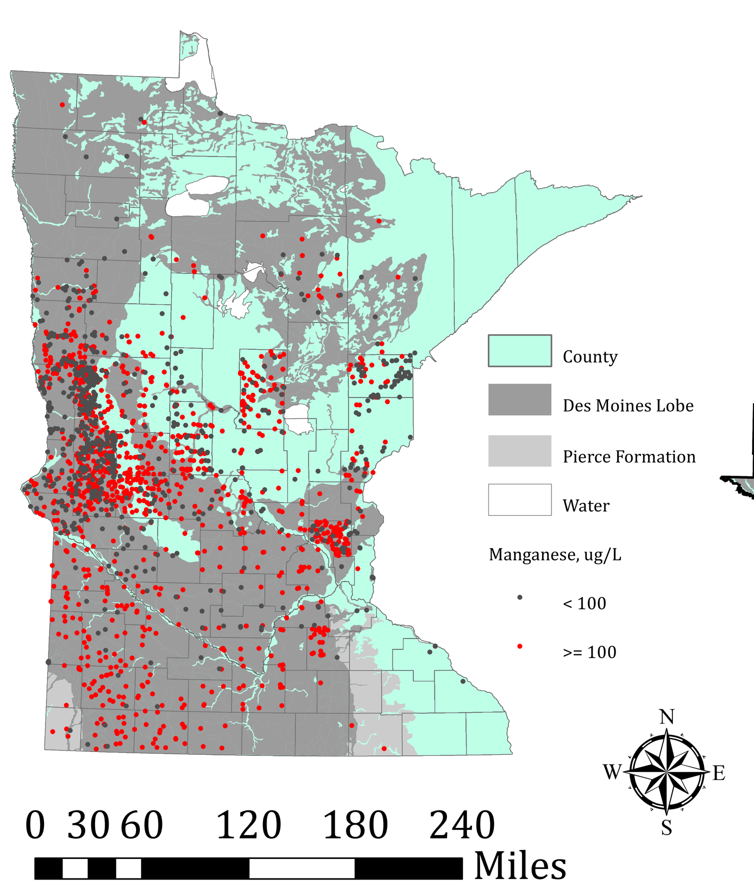


Figure 2. Manganese concentrations in source water collected from 1953 location-verified drinking water supply wells completed in the Quaternary buried artesian aquifer (QBAA or QBUA). Aquifers as determined by County Well Index. Geology by MGS.

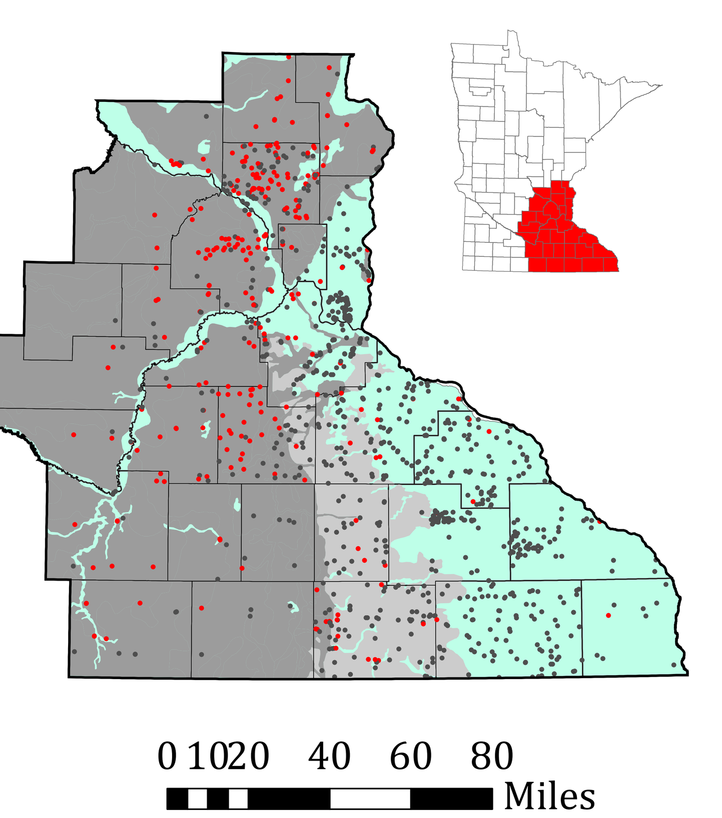


Figure 3. Manganese concentrations in source water from 1085 location-verified drinking water supply wells completed in Paleozoic bedrock aquifers. Aquifers as determined by County Well Index. Geology by MGS.

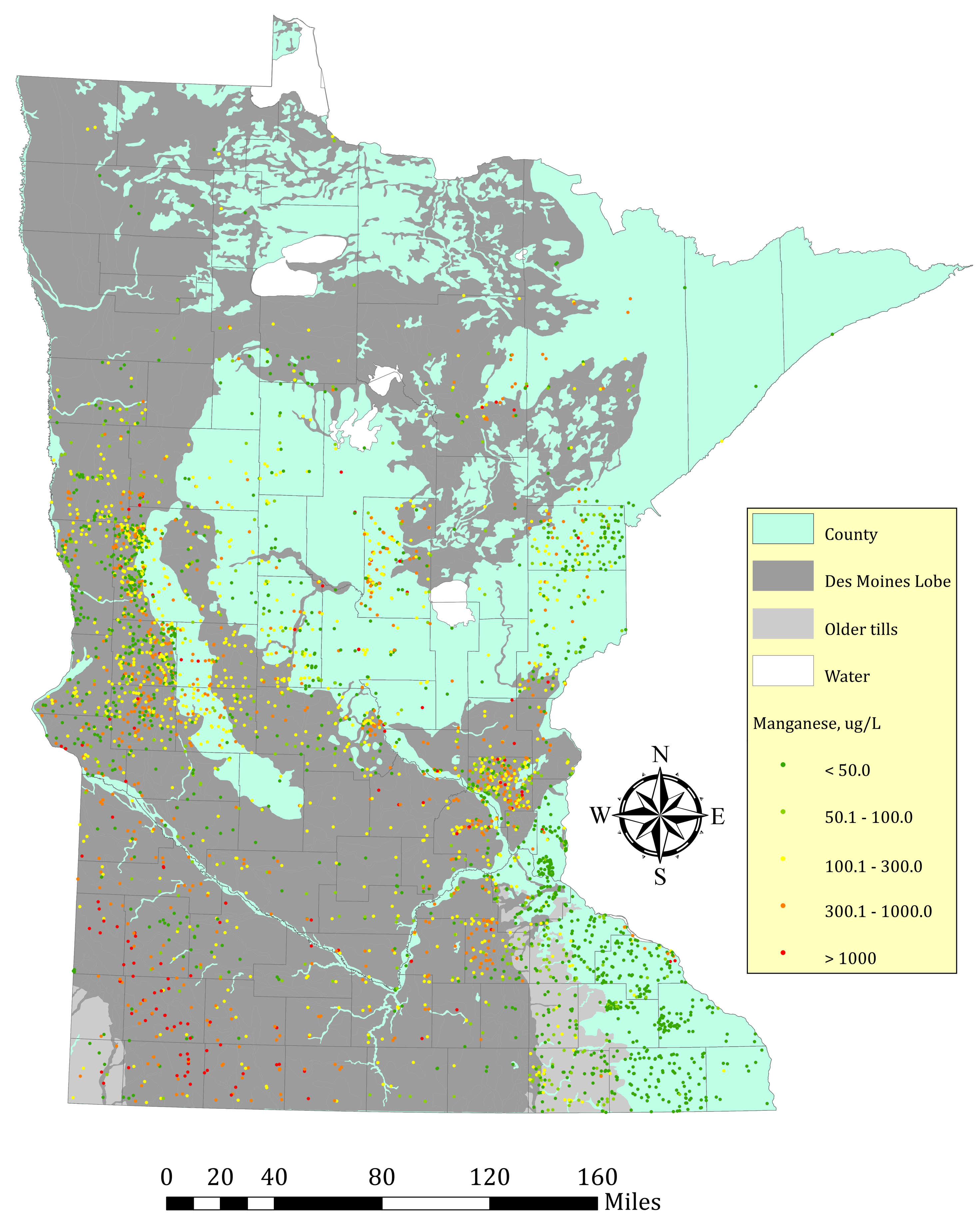


Figure 1. Manganese concentrations in source water collected from 3802 location-verified drinking water supply wells. Geology by Minnesota Geological Survey (MGS).

Manganese concentrations exceed 100 ug/L in 63% of wells in buried artesian aquifer settings. A belt of approximately 100 wells with concentrations greater than 1000 ug/L occurs in southwestern Minnesota. In Paleozoic bedrock aquifers, concentrations are generally less than 100 ug/L. Wells with the highest concentrations occur along the western Paleozoic boundary, near the likely regional recharge zone.

Manganese and casing material. Manganese concentrations were higher in plastic-cased wells than in metal-cased wells. It is unlikely that plastic casing causes higher manganese concentrations. However, it is possible that metal casing promotes scavenging of manganese as water passes through the screen. In this case the scavenged manganese may precipitate on well components as scale.

Manganese and unconfined hydraulic conditions. Oxygenated conditions were expected to produce low manganese concentrations. Higher manganese concentrations were expected to occur in deeper wells screened in the anoxic part of the water table aquifer. However, a plot of manganese concentration versus distance between the top of the screen and water table showed no obvious correlation.

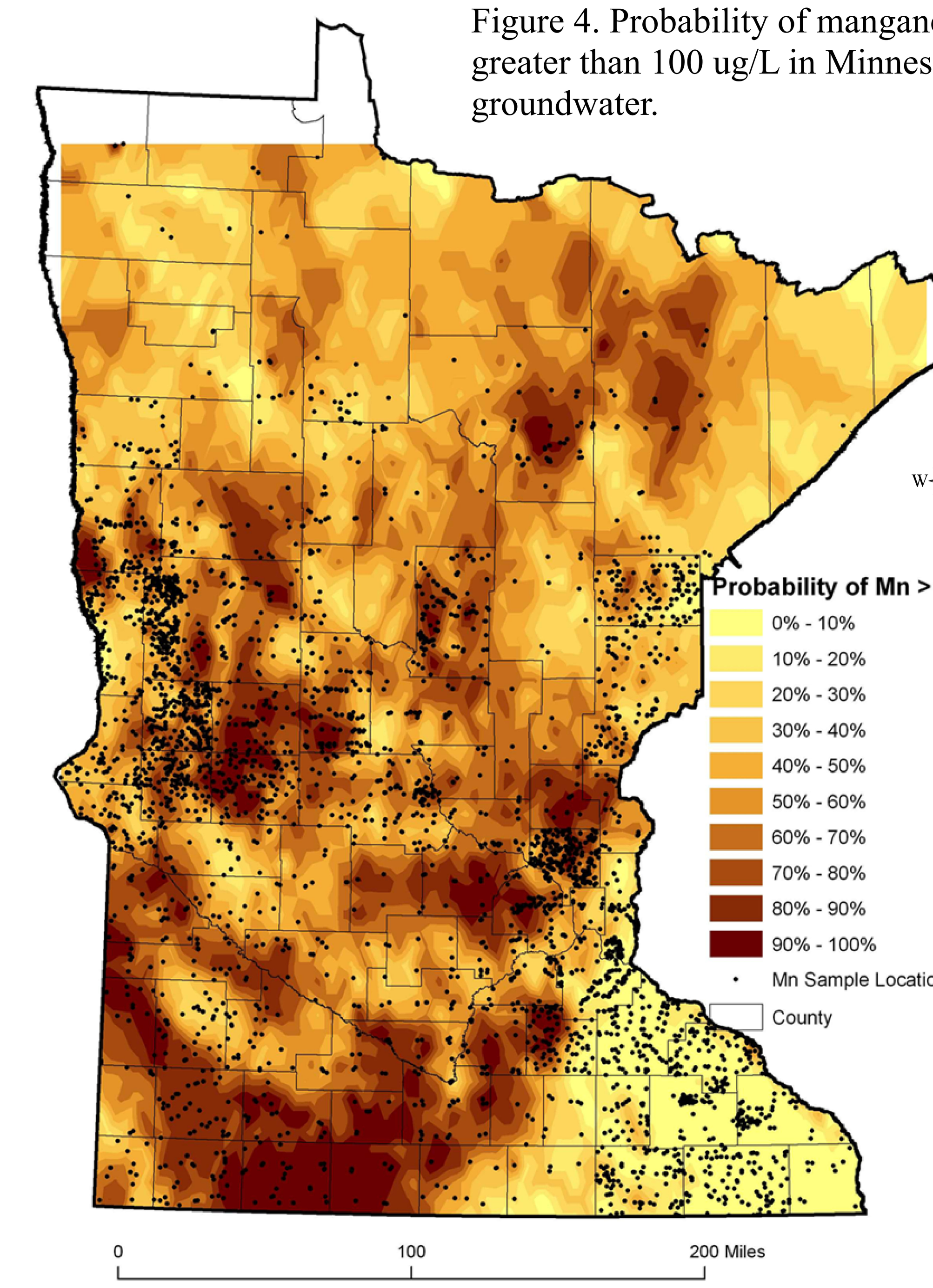
Table 1: Descriptive Statistics, Manganese, by Aquifer

Aquifer	N	Min	Max	Median	Mean	STDEV
Quaternary WT	331	0.1	2677	155	310	451
Buried Artesian	1969	0	3620	160	269	378
Cretaceous	117	0.4	3213	53	232	504
Paleozoic	1104	0	2050	32	98	193
All	4339	0	5040	93	214	356

Table 2: Wells Exceeding MCL or HRL

Aquifer	Exceed MCL (number)	Exceed MCL (%)	Exceed HRL (number)	Exceed HRL (%)
Quaternary WT	207	62.5	187	56.5
Buried Artesian	1466	74.5	1240	63.0
Cretaceous	62	53.0	43	36.8
Paleozoic	437	39.6	268	24.3
All	2667	61.5	2123	48.9

Figure 4. Probability of manganese greater than 100 ug/L in Minnesota groundwater.



Spatial correlation. Manganese concentrations were converted to indicator values ("1" or "0"), allowing data analysis to be independent of the frequency distribution, and averages to represent probabilities of exceeding the threshold. This procedure determined a strong spatial correlation, with a range (1,500 meters) similar in scale to glacial sand aquifer thickness and hydraulic conductivity.

Conclusions and Recommendations

This initial assessment provides large-scale context on the problem of manganese in Minnesota groundwater, and supports the following conclusions:

- Manganese distribution is highly variable but there are areas where concentrations are consistently less than 50 ug/L (southeastern Minnesota) or greater than 1,000 ug/L (southwestern Minnesota). The southwestern area of elevated concentrations roughly corresponds to the western flank and interior of the Des Moines Lobe till.
- Manganese concentrations in plastic-cased wells were twice those in steel-cased wells, consistent with a manganese-removal mechanism specific to steel-cased wells.
- For wells completed in water table settings, no correlation was determined between manganese concentration and screen placement below static water level.
- The manganese data were strongly spatially correlated.

The best strategy for increasing our understanding of manganese in groundwater will be continued analysis of existing data combined with targeted geochemical assessments over restricted areas of interest where geology and hydrogeology are well-constrained.

References

Fong, Alison L., Andrews, William J., and Stark, James R., (1998), *Water-quality assessment of part of the upper Mississippi River Basin, Minnesota and Wisconsin—Ground-water quality in the Prairie du Chien-Jordan Aquifer, 1996*, USGS Water-Resources Investigations Report 98-4248, 45 pp.

Hem, John D., (2005), *Study and interpretation of the chemical characteristics of natural water*, USGS Professional Paper 1473 (reprinted from 1970 edition), 363 pp.

Lively, Richard S., Jameson, Roy, Alexander, E.C., Jr., and Morey, G.B., (1992), *Radium in the Mt. Simon-Hinckley aquifer, east-central and southeastern Minnesota*, Minnesota Geological Survey Information Circular 36, 58 pp.

Marsh, Richard, (1997), *Evaluation of trace metals and sulfates in individual water supplies, Anoka County, Minnesota,* Anoka County Comm. Health and Env. Serv. Dept., 50 pp.

MDH (Messing R., R. Soule, J. Small-Johnson, D. Durkin, M. Salisbury (née Erickson), L. Souther, J. Connett, B. Baker). December 2001. The Minnesota Arsenic Study (MARS): Final Report to Agency for Toxic Substances and Disease Registry (ATSDR).

MDH, (2011), County Well Index (CWI) database of well construction and geologic data, data downloaded December 2011.

MDH, (2011), Minnesota Drinking Water Information System (MNDWIS), drinking water quality data downloaded on December 16, 2011.

MDNR CGA WQ datasets, downloadable from: http://www.dnr.state.mn.us/waters/groundwater_section/mapping/chemdataaccess.html

MPCA, Ground Water Monitoring and Assessment Program (GWMAP) dataset, http://www.pca.state.mn.us/index.php/water/water-types-and-programs/groundwater/groundwater.html

Smith, E.S., and Nemetz, D.A., (1996), *Water quality along selected flowpaths in the Prairie du Chien-Jordan Aquifer, southeastern Minnesota,* USGS Survey Water-Resources Investigations Report 95-4115, 76 pp.

Wall, D.B., and Regan, C.P., (1994), *Water quality and sensitivity of the Prairie du Chien-Jordan Aquifer in west-central Winona County,* MPCA, Water Quality Division, 65 pp.