Memo

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To: Manganese Group

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Subject: Initial Assessment of Manganese in Minnesota Groundwater

Minnesota Department of Health (MDH) 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) remains 100 ug/L. Because of concerns related to source water used in baby formula, MDH may soon apply these federal and state drinking water quality standards more widely than in the past. According to MDH health risk assessors, there is evidence of observed health effects due to the presence of manganese in drinking water at concentrations exceeding 300 ug/L. Because little is known about the natural distribution of manganese in Minnesota groundwater, the MDH Source Water Protection (SWP) program prepared the following summary.

Background Information on Manganese in the Subsurface

Background information is summarized from Hem (2005), a standard general reference for geochemistry of natural waters. The geochemical properties of manganese and iron are often considered together. Although these metals behave similarly in the environment, there are important differences. Manganese is much less abundant than iron in the earth's crust, but still widely distributed in rocks and soil. Biotite and hornblende minerals usually contain some manganese. Manganese commonly occurs in the Mn^{+2} (reduced) form, less commonly as Mn^{+4} (the Mn^{+3} ion is uncommon in water). These manganese oxide and hydroxide ions strongly adsorb to metallic cations, forming coatings on mineral surfaces. Manganese is much slower to precipitate than iron. Groundwater containing more manganese than iron is uncommon.

The Minnesota Pollution Control Agency (MPCA) conducted the Ground Water Monitoring and Assessment Program (GWMAP) in the early to mid-1990s to assess the hydrogeochemistry of natural waters throughout the state. Manganese (along with nitrate, iron, arsenic, and boron) was strongly correlated to oxidation-reduction potential (redox) conditions in groundwater. Manganese concentrations increased as redox potential decreased.

Manganese Data Sets

MDH possesses several datasets containing total (verified or assumed to be unfiltered, field-acidified) manganese data. Laboratory analytical methods and detection limits vary among the datasets. The manganese datasets used in the initial assessment originated from the following sources:

- MDH
  - Minnesota Drinking Water Information System (MNDWIS), general chemistry in source water from community public water supply wells, various sampling dates, database downloaded December 2011, N = 250.
  - MNDWIS, general chemistry collected by SWP, various sampling dates, database downloaded December 2011, N = 150.
  - Minnesota Arsenic Research Study (MARS) data set (MDH, 2001), various sampling dates in the late 1990s, N = 893.
- Minnesota Pollution Control Agency (MPCA)
  - GWMAP, various sampling dates in the early-to-mid 1990s, N = 1319.
  - Wall and Regan, 1994, sampling conducted in 1990 and 1991, N = 42.
- United States Geological Survey (USGS)
  - USGS Water-Resources Investigation WRI 98-4248 (Fong, et al., 1998), sampling conducted 1994-1998, N = 11.
  - USGS Water-Resources Investigation WRI 95-4115 (Smith and Nemetz, 1995), sampling conducted in 1990 and 1991, N = 130.
- Minnesota Geological Survey (MGS)
  - Lively, et al., 1992, sampling conducted in 1989 and 1990, N = 71.
- Anoka County
  - Anoka County Trace Metals Study, 2004, samples collected in 199, N = 190.
- Minnesota Department of Natural Resources (MDNR)
  - County Geologic Atlas water quality data set, various sampling dates 1980s to present, N = 1316.

For wells sampled on more than one date, the greatest available analytical result was selected, with the following exceptions:

- For a newly-drilled well, the initial manganese concentration was commonly much higher than subsequently measured concentrations, sometimes by an order of magnitude or more. In these cases anomalously elevated data points were neglected and a representative value was selected from remaining analytical results.
- In cases where the analysis indicated “not detected” or “below detection,” the lowest detection limit was selected as most accurate and, therefore, representative.

Description of Manganese in Groundwater

Simple descriptive statistics (Table 1) reveal a statewide distribution of 4339[1] data points, with a mean manganese concentration of 214 ug/L, a median of 93 ug/L, and a standard deviation of 356 ug/L. The data define a skewed, log-normal frequency distribution. Manganese concentrations ranged from below detection to 5,040 ug/L (which occurred in a well for which there was no geologic data and so the aquifer was unknown). Quaternary water table (WT) and buried artesian aquifer settings have the greatest median manganese concentrations (155 and 160 ug/L, respectively), and the Paleozoic bedrock aquifers had the least (32 ug/L).

Table 2 indicates that samples at a total of 2,667 wells (61.5%) exceeded the MCL of 50 ug/L, and samples at 2,123 wells (48.9%) exceeded the manganese HRL of 100 ug/L. The 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%).

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

Aquifer information source: County Well Index

Table 2: Wells Exceeding Secondary MCL (50 ug/L) and HRL (100 ug/L)

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

Figures 1 through 5 are maps showing the spatial distribution of available manganese data for various aquifer settings. Figure 1 shows the entire data set in five manganese concentration classifications partly based on existing standards (50 ug/L, 100 ug/L). Figure 2 depicts manganese concentrations above or below the HRL (100 ug/L). Figures 3, 4 and 5 show manganese concentrations above or below the HRL only for wells completed within water table conditions, Quaternary buried artesian aquifers, and Paleozoic bedrock aquifers, respectively.

[1] Two data points with very high manganese concentrations (406,000 ug/L and 24,313 ug/L) were likely due to unintended inclusion of solid material in the sample. These two results were deleted from the assessment.

Discussion

Statewide distribution of manganese. The highest data density occurs in the northern Twin Cities metropolitan area, and the lowest data density is in northeastern and northwestern Minnesota (Figures 1 and 2). Manganese concentrations vary widely across the state, especially in areas with high data density, suggesting a complex mechanism for manganese occurrence. Figures 3-5 portray the following patterns of manganese occurrence, by aquifer:

- In Quaternary water table (QWTA) settings, 56.5% of drinking water wells have manganese concentrations greater than 100 ug/L.
- In Quaternary buried artesian (QBAA and QBUA) aquifer settings, 63.0% of drinking water wells have manganese concentrations greater than 100 ug/L. A belt of approximately 100 wells with very high (greater than 1000 ug/L) manganese concentrations occurs in southwestern Minnesota.
- In Paleozoic bedrock aquifers of southeastern Minnesota, manganese concentrations are generally less than 100 ug/L. Wells with the highest manganese concentrations are located along the western Paleozoic boundary, within or near the likely regional recharge zone.

Manganese and casing material. Due to well code requirements, wells with plastic casing are likely to be relatively shallow and, consequently, were expected to yield relatively oxygen-rich water with lower manganese concentrations. To test for this, manganese concentrations were compared to casing material: steel (galvanized, cast iron, stainless steel, or black/low carbon steel) versus plastic.

Table 3: Casing material and manganese concentration, ug/L

Casing Material	Mean	Median	Range	Standard Deviation	N
Metal	185	65	0-3550	327	2260
Plastic	258	153	0-5040	394	1670

"Metal" includes galvanized iron, cast iron, stainless steel, and black or low carbon steel.

The comparison yielded the unexpected result that mean and median manganese concentrations were higher in plastic-cased wells than in metal-cased wells. It is unlikely that plastic casing causes an increase in 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. Water table aquifers of limited thickness may be relatively well mixed with respect to dissolved oxygen, geochemically limiting the release of manganese into solution. However, dissolved oxygen may stratify in water table aquifers with significant saturated thickness, a geochemical condition that may enhance the release of available manganese into solution. We compared manganese concentrations to screen-top depth below water table for QWTA wells. Wells screened within the high-dissolved oxygen portion of the aquifer (e.g., across the water table or within a few feet of it) were expected to produce low manganese concentrations. Higher manganese concentrations were expected to occur in wells screened in the anoxic part of the water table aquifer, but more deeply placed beneath the water table. However, a plot of manganese concentration versus distance between the top of the screen and water table showed no obvious correlation.

Spatial correlation. To geostatistically assess the spatial relationships within the manganese data set, raw manganese concentrations were converted to indicator values (a value of 1 if above 100 ug/L and 0 if below). This procedure allowed data analysis to be independent of the frequency distribution, and for averages to be interpreted as 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 (Figure 6).

Manganese and depth below a confining layer. One idea that is gaining acceptance relies on emerging evidence that arsenic concentrations may depend on the well screen placement with respect to the bottom confining layer contact. Because of its geochemical similarity to arsenic, the manganese data was also examined for control by screen placement below the confining unit. The data in this report did not bear out any similar promising hypothesis for the relationship between manganese occurrence (greater than 100 ug/L) and screen placement (Figure 7). Most of the confidence intervals on Figure 7 overlap with adjacent points, suggesting that screen length is a factor that may need further assessment.

Conclusions and Recommendations

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

1. The statewide manganese distribution in groundwater 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.
2. Manganese concentrations in plastic-cased wells were twice those in steel-cased wells. This finding is consistent with a manganese-removal mechanism specific to steel-cased wells.
3. For wells completed in water table settings, there was no strong correlation between manganese concentration and screen placement below static water level.
4. The manganese data were strongly spatially correlated.
5. In contrast to arsenic, there appears to be no obvious relationship between screen placement and the occurrence of elevated manganese. However, screen length is a potential factor that may need further assessment.

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. Some examples of analytical methods and factors that could be assessed include:

- Statistical tools
  - Re-evaluate manganese concentration data using detection limit information to determine an accurate frequency distribution model.
  - Analysis of variance (ANOVA) or paired analysis to determine the relative importance of well construction and/or geologic factors suspected of playing a role in manganese occurrence (see below).
- Well construction factors
  - Well diameter, well yield; high capacity (community wells) versus low-capacity (noncommunity or domestic) wells.
  - Paired analysis of closely-spaced wells in the same aquifer with differing casing materials (e.g., metal versus plastic).
  - Compare manganese concentration to estimated metallic surface area in wells.
- Geologic factors
  - Compare manganese concentration to hydrogeologic setting.
  - Determine the hydrogeochemical relationship between manganese concentration and other trace metals (arsenic) or dissolved oxygen.
- Temporal factors
  - Conduct short interval time-series sampling study (1 min, 3 min, 5 min, 10 min, etc) at selected wells to determine whether elevated manganese is related to manganese-containing casing scale material dislodged in early pumping.
  - Sample newly-installed wells where elevated manganese concentrations are expected to determine 1) changes over times; and 2) if the rate of change is consistent with predictions by geochemical models.

The manganese dataset continues to grow. Sampling efforts for including manganese that are in the planning stages or underway include:

- Noncommunity public water supply program.
- Domestic well study (MDH well management sampling proposal).
- General chemistry sampling program at community PWS wells.
- MPCA ambient groundwater monitoring program.
- Planned extension of the Volunteer Nitrate Monitoring Network monitoring project.

Unique opportunities exist to communicate findings for information gathered at certain wells, for instance noncommunity public water supply wells at locations such as state parks and Minnesota Department of Transportation (MNDOT) rest stops. In these locations the importance of the findings could be communicated publicly through the use of kiosks or displays explaining results.

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***, United States Geological Survey Water-Resources Investigations Report 98-4248, 45 pp.

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Marsh, Richard, (1997), ***Evaluation of trace metals and sulfates in individual water supplies, Anoka County, Minnesota,*** Anoka County Community Health and Environmental Services Department, 50 pp.

Minnesota Department of Health (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).

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

Minnesota Department of Health, (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

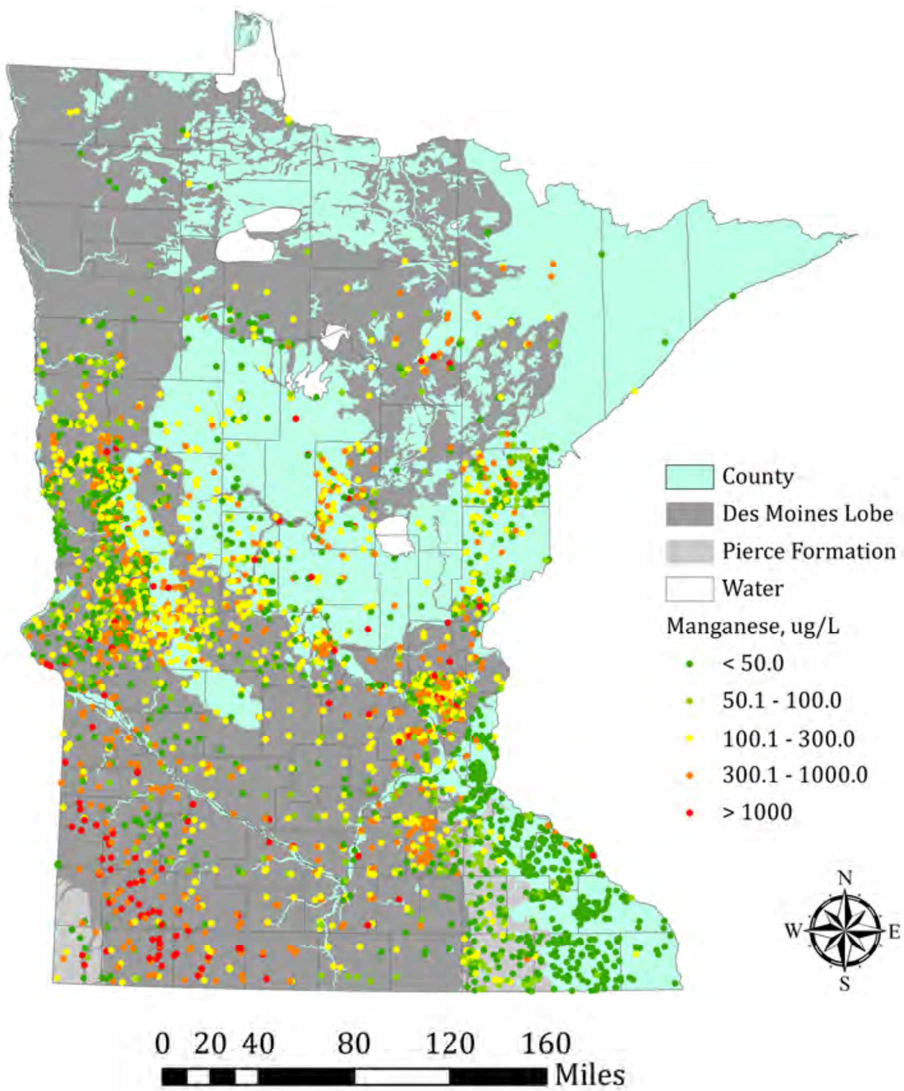
Minnesota Pollution Control Agency, Ground Water Monitoring and Assessment Program (GWMAP) dataset, http://www.pca.state.mn.us/index.php/water/water-types-and-programs/groundwater/groundwater.html

Smith, E.S., and Nemetz, D.A., (1996), ***Water quality along selected flowpaths in the Prairie du Chien-Jordan Aquifer, southeastern Minnesota,*** United States Geological 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,*** Minnesota Pollution Control Agency, Water Quality Division, 65 pp.

Figure 1: Manganese Concentrations: All Aquifers

Map prepared by Minnesota Department of Health, June 2012

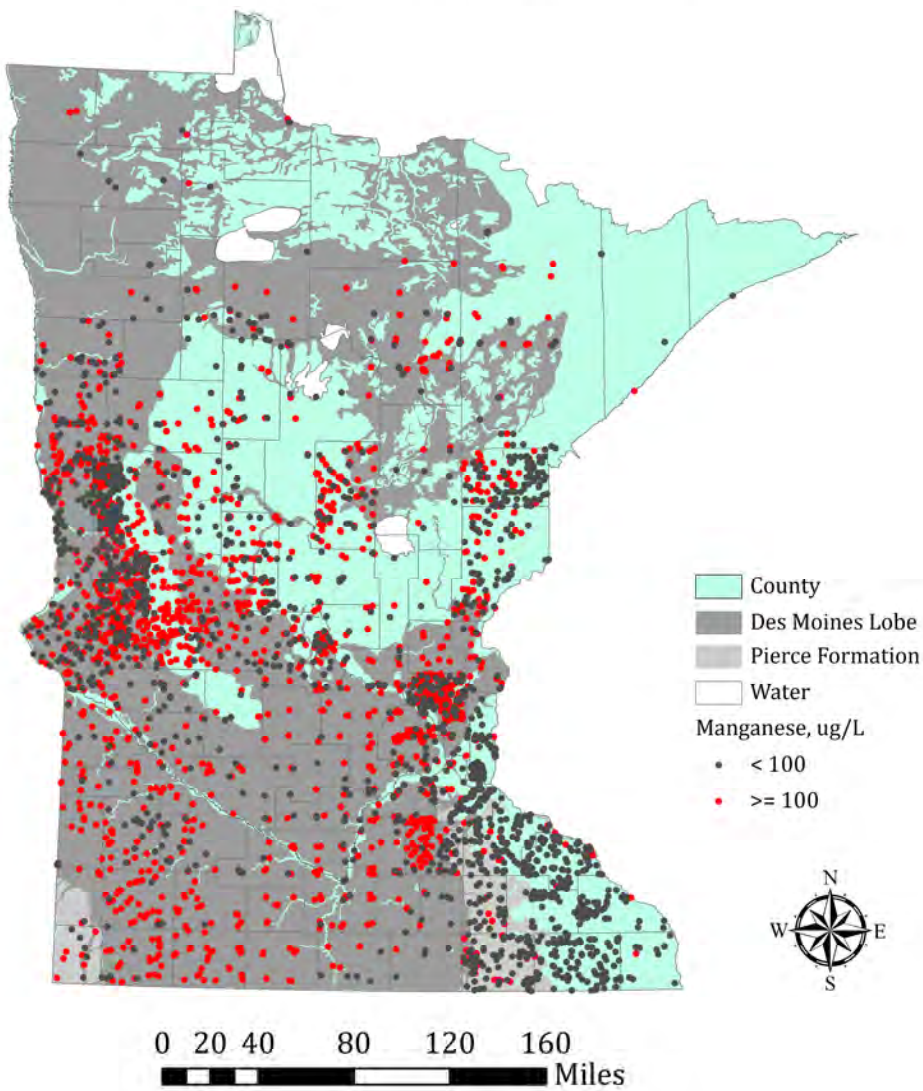


Manganese concentrations for 3802 location-verified drinking water supply wells. Geology by Minnesota Geological Survey.

Data sources: Minnesota Department of Health, Minnesota Pollution Control Agency, Minnesota Department of Natural Resources, Minnesota Geological Survey, United States Geological Survey, and Anoka County.

Figure 2: Manganese Concentrations Greater Than Versus Less Than 100 ug/L: All Aquifers

Map prepared by Minnesota Department of Health, June 2012

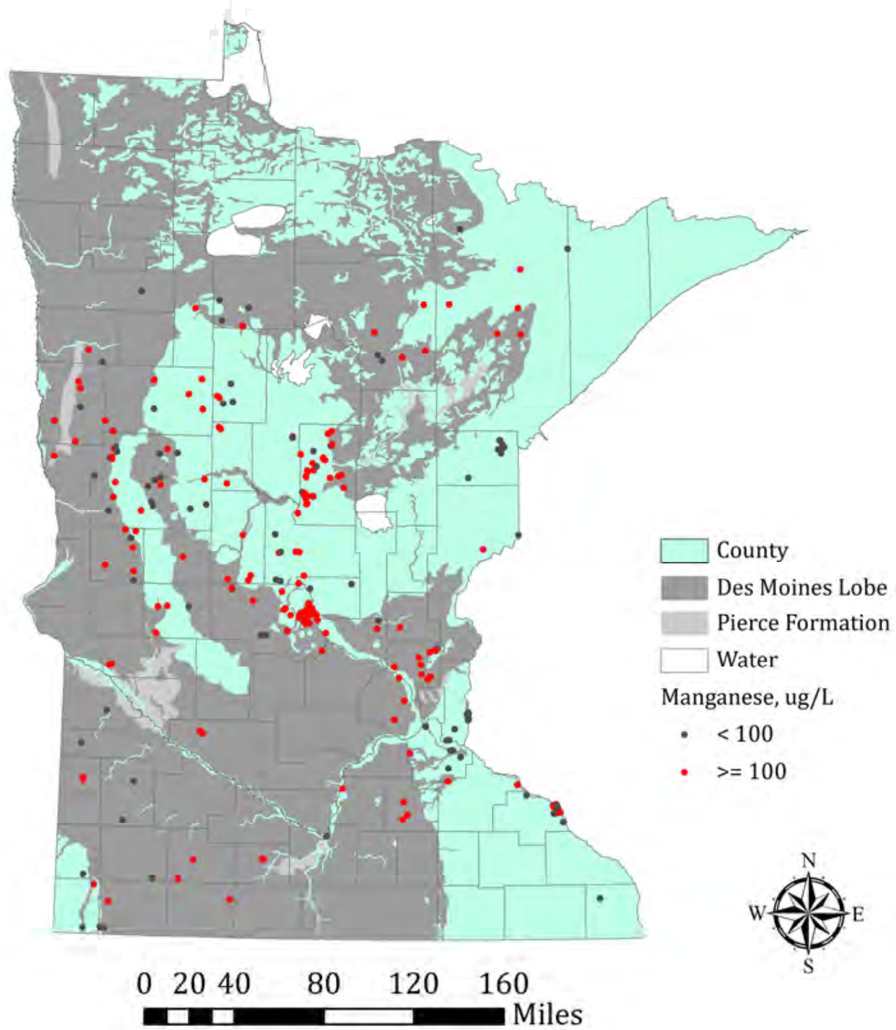


Manganese concentrations in source water collected from 3802 location-verified drinking water supply wells. Geology by Minnesota Geological Survey.

Data sources: Minnesota Department of Health, Minnesota Pollution Control Agency, Minnesota Department of Natural Resources, Minnesota Geological Survey, United States Geological Survey, and Anoka County.

Figure 3: Manganese Concentrations in Water Table Settings

Map prepared by Minnesota Department of Health, June 2012

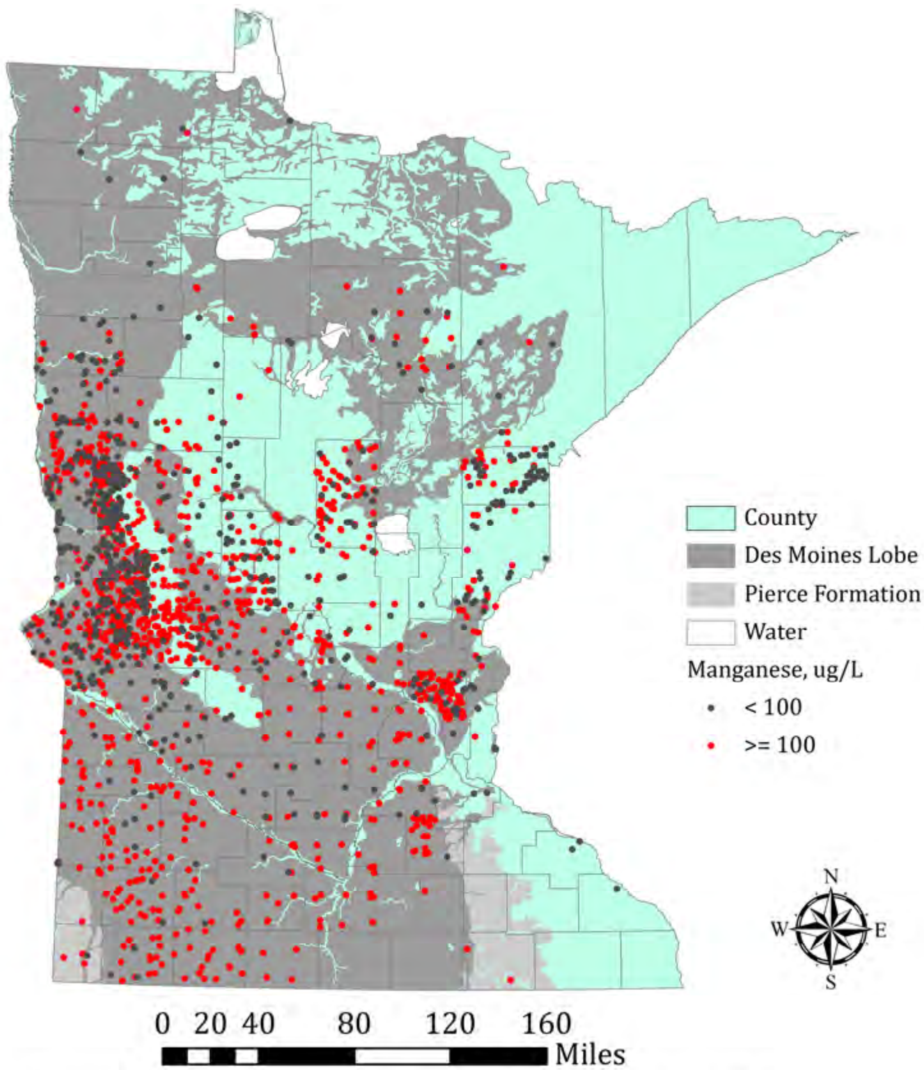


Manganese concentrations in source water collected from 298 location-verified drinking water supply wells completed in the water table aquifer (QWTA). Aquifers as determined by County Well Index. Geology by Minnesota Geological Survey.

Data sources: Minnesota Department of Health, Minnesota Pollution Control Agency, Minnesota Department of Natural Resources, Minnesota Geological Survey, United States Geological Survey, and Anoka County.

Figure 4: Manganese Concentrations in Quaternary Buried Artesian Aquifer Settings

Map prepared by Minnesota Department of Health, June 2012

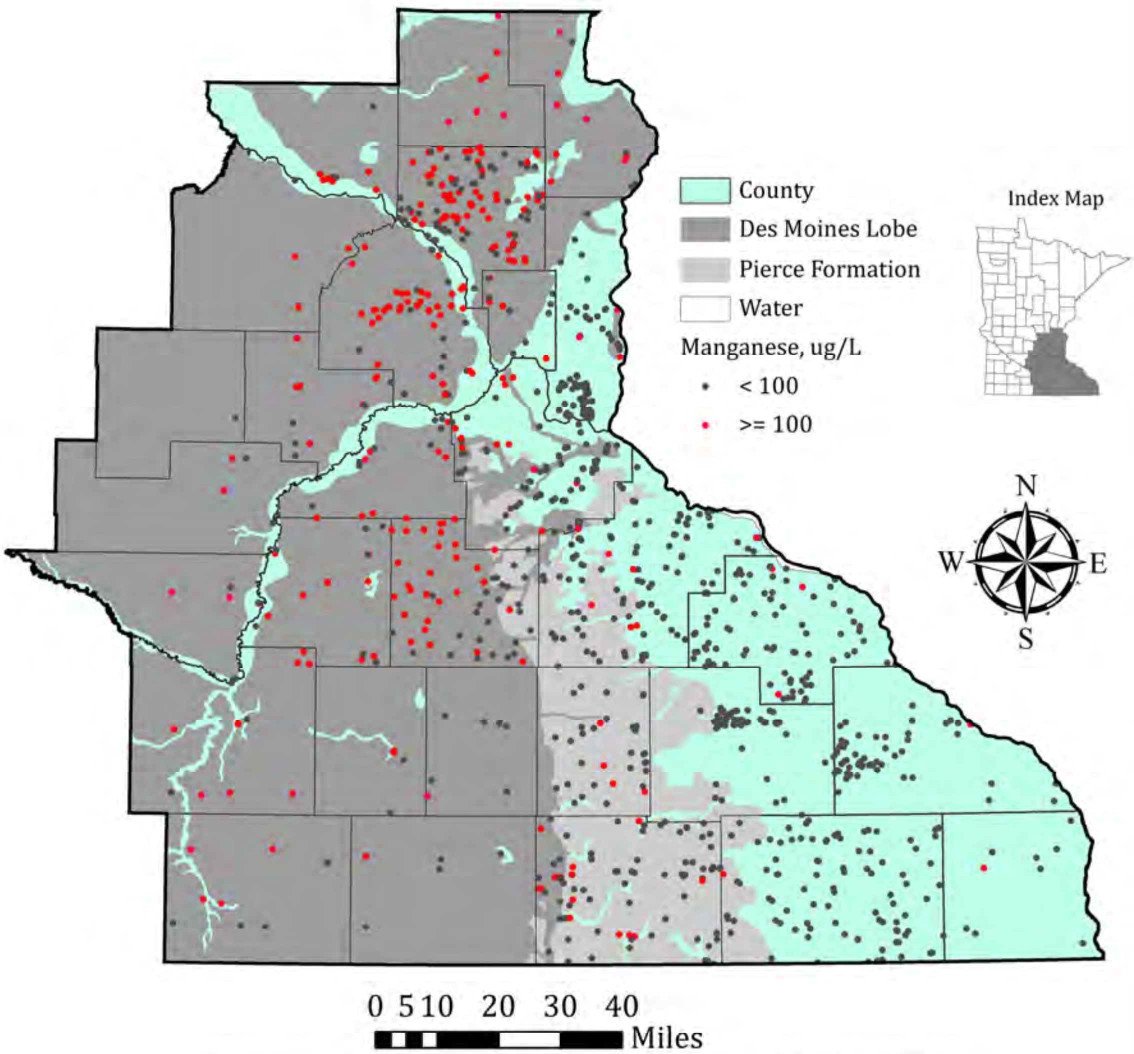


Manganese concentrations in source water collected from 1953 location-verified drinking water supply wells completed in the Quaternary buried artesian aquifer (QBAA or QBUA). Aquifers as determined by County Well Index. Geology by Minnesota Geological Survey.

Chemistry data sources: Minnesota Department of Health, Minnesota Pollution Control Agency, Minnesota Department of Natural Resources, Minnesota Geological Survey, United States Geological Survey, and Anoka County.

Figure 5: Manganese Concentrations: Paleozoic Bedrock Aquifer Settings

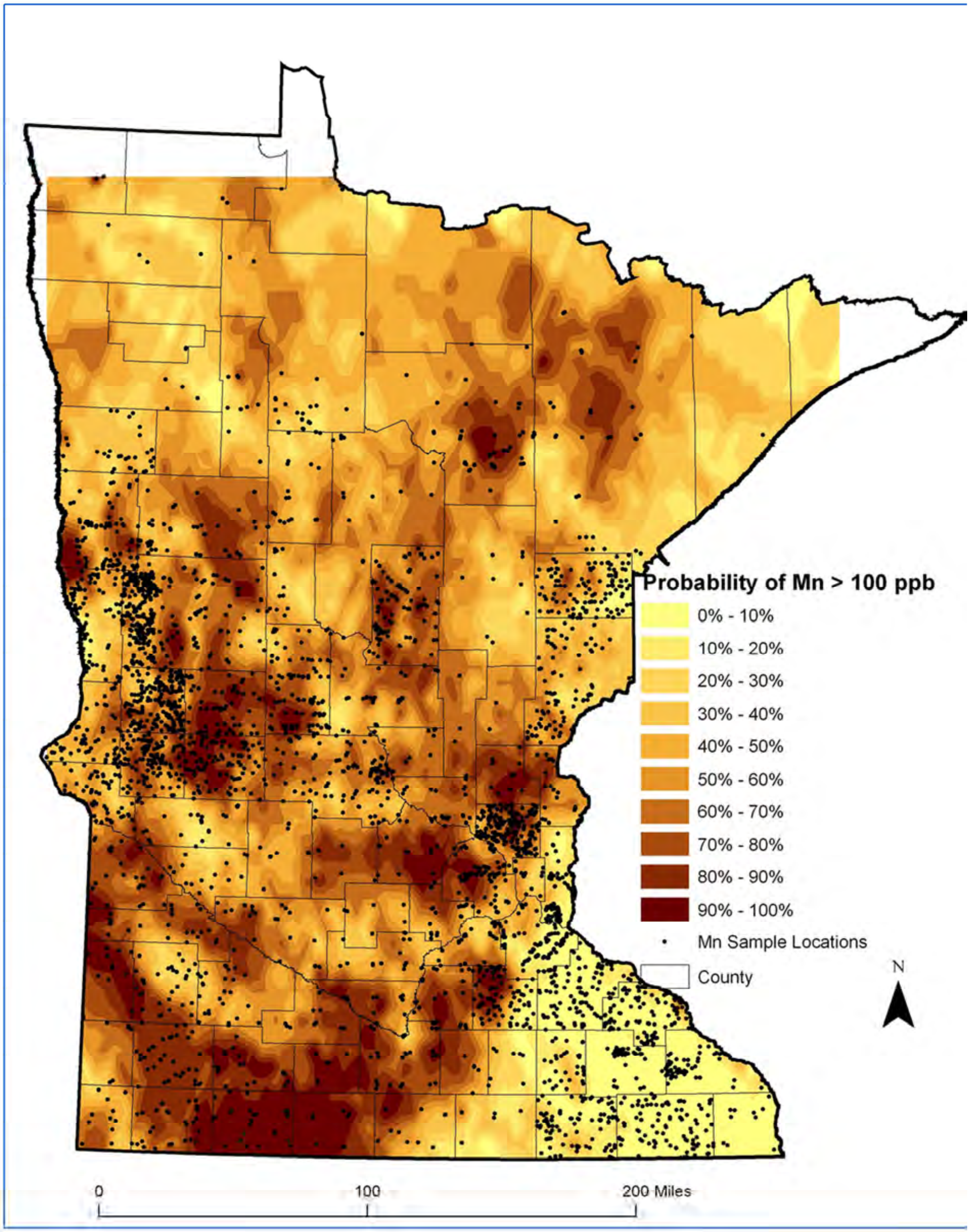
Map prepared by Minnesota Department of Health, June 2012

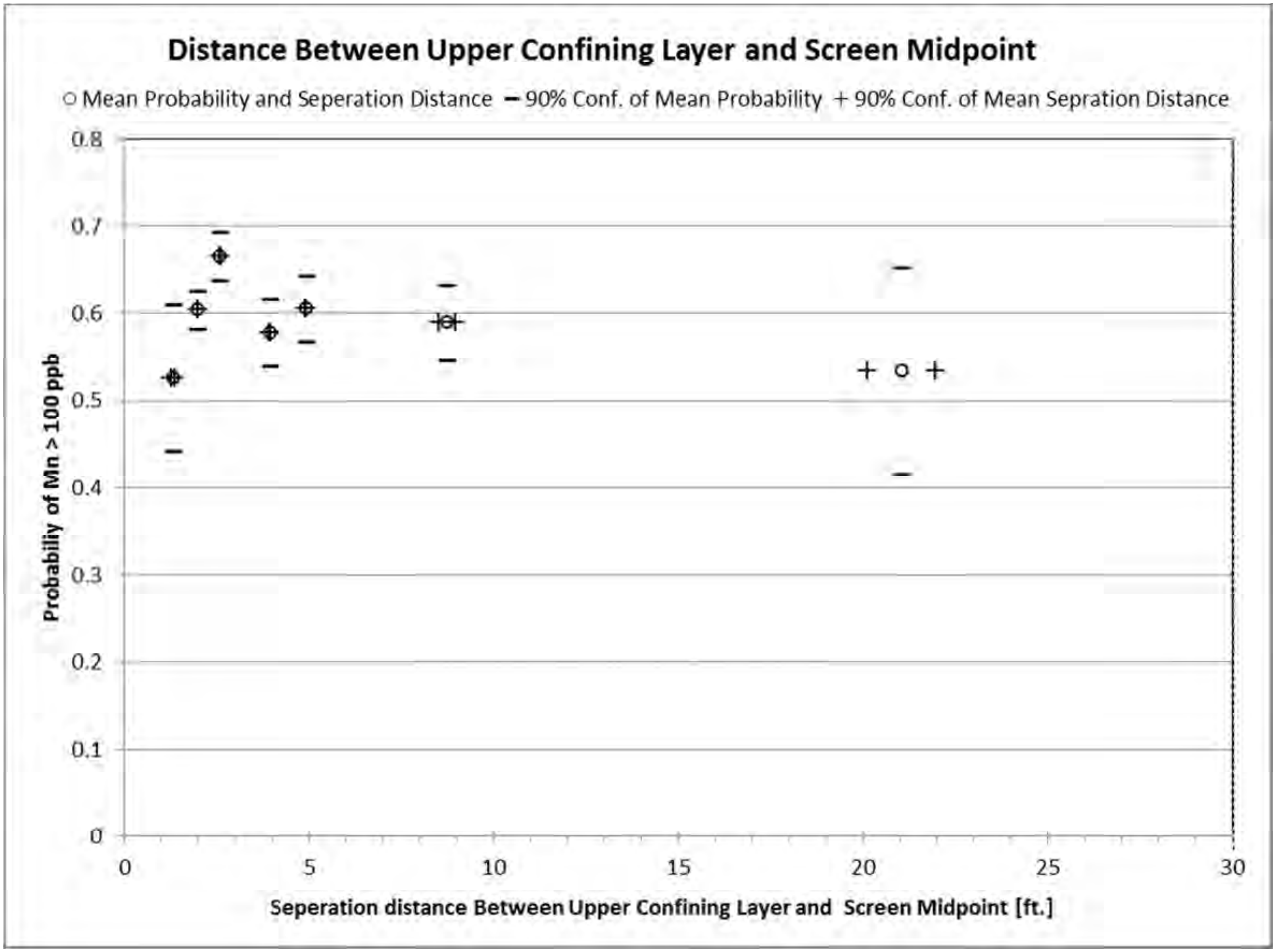


Manganese concentrations in source water collected from 1085 location-verified drinking water supply wells completed in the Paleozoic bedrock aquifer. Aquifers as determined by County Well Index. Geology by Minnesota Geological Survey.

Chemistry data sources: Minnesota Department of Health, Minnesota Pollution Control Agency, Minnesota Department of Natural Resources, Minnesota Geological Survey, United States Geological Survey, and Anoka County.

Figure 6: Probability of Manganese Greater Than 100 ug/L in Minnesota Groundwater




Distance Between Upper Confining Layer and Screen Midpoint
○ Mean Probability and Seperation Distance
— 90% Conf. of Mean Probability
+ 90% Conf. of Mean Sepration Distance
Probabiliy of Mn > 100 ppb
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
Seperation distance Between Upper Confining Layer and Screen Midpoint [ft.]