

**MINNESOTA GEOLOGICAL SURVEY**  
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**MINNESOTA SOIL, TILL, AND GROUND-WATER GEOCHEMICAL DATA**

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This document, and the associated atlas, poster, and data files are accessible from the web site of the Minnesota Geological Survey (<http://www.geo.umn.edu/mgs/>) as PDF and Excel files, as well as an ESRI geodatabase.

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# MINNESOTA SOIL, TILL, AND GROUND-WATER GEOCHEMICAL DATA

## ABSTRACT

R.S. Lively and L.H Thorleifson

The rocks and soils that are the foundation of our environment leave an imprint on the chemistry of our water and our lives. This chemical landscape reflects a combination of natural history and cumulative human impacts, and it influences biodiversity and human health. Geochemical mapping thus is needed to clarify elemental variations, and to support assessment of the natural and human-influenced factors that dictate these variations. The Minnesota Geological Survey (MGS) and the Minnesota Pollution Control Agency (MPCA), in cooperation with the United States Geological Survey (USGS), therefore have assembled three geochemical data sets for soil and water as a basis for an atlas that will provide an overview of geochemical patterns, and a reference that will place more thorough environmental geochemical surveys into a context. Data contributed to the project were derived from soil, soil parent material, and well water samples analyzed following USGS, Geological Survey of Canada, and Environmental Protection Agency protocols, respectively. The soil data include stream sediments largely in the western part of the state, and the soil parent material data are from sites underlain by till. The well water samples were from multiple aquifers utilized for drinking water, at greatly varying depth and geology.

The analyzed fraction for soils was <150 microns, for soil parent materials it was <63 microns, and both employed a multi-acid near-total digestion. Soil geochemistry data, provided by the USGS, were derived from 1,352 samples. Maps were prepared by averaging the results from soil in the top 0.2 meter and at about 0.5 meter depth from the same sample site. The stream sediment data included in the soil maps were from west-central and western Minnesota, and a few additional samples in other parts of the state. Soil and some stream sediments were collected in 2004 and 2005. Most stream sediments were collected in 1979, under the National Uranium Resource Evaluation program, and were reanalyzed by the USGS in 2005. Results for soil parent material were from 250 till samples collected at 1 to 2 meters depth that were analyzed as part of an indicator mineral survey conducted in 2004. The ground-water data provided by the MPCA were based on 954 water well samples collected between 1993 and 1996. The water well sampling was conducted in a nine square mile cell on 11-mile centers, within which one sample was collected from each identified aquifer used as a source of drinking water.

Atlas pages were prepared for each variable, with maps for each sampling medium on a single page, along with a generalized explanation. Symbol categories were based on natural groupings in the data using the natural breaks method; values below detection were set to half the detection limit. The data tables for each medium are available as Excel tables and as an ESRI geodatabase. Selected element maps and general geologic information are also presented as a poster to give an overview of the geochemical landscape and a basis for its interpretation in relation to geology. Together, the tables and database components provide a regional reference for environmental management and exploration that will typically rely on more detailed sampling. Construction of the atlas was funded by the Minnesota Minerals Coordinating Committee. The maps, poster, and data are available from the Minnesota Geological Survey web site, and additional information may be obtained from the MPCA and the USGS.

## **INTRODUCTION**

Minnesota is a large state with varied geology. Geologic materials at the land surface play a role in agriculture, public health, mineral exploration, and environmental management. Although there has been much focused geochemical assessment in and around Minnesota, there remains a need for a regional overview of geochemistry to provide context for site-specific exploration and environmental investigations. Some national geochemical information has, for some time, been available from the USGS for a limited number of elements, and from sample spacing of ~75 km (Shacklette and Boerngen, 1984; Gustavsson et al., 2001).

An opportunity to compile geochemical datasets for Minnesota resulted from: 1) completion of a statewide indicator mineral and geochemical survey by MGS, in cooperation with industry, that sampled soil parent materials where they consist of till; 2) systematic sampling and analysis of soils and stream sediments across Minnesota by the USGS, with the participation of MGS; and 3) cooperation with the MPCA to incorporate existing Minnesota ground-water chemistry data with the soil data. Each of the data sets has a statewide distribution and samples from each project were analyzed by separate laboratories following consistent and documented protocols for the media sampled.

The following steps were undertaken: assembly of soil and stream sediment data produced by the USGS, till geochemical data produced by MGS, and ground-water data produced by MPCA into an ESRI geodatabase format; production of page-size monochrome atlas pages depicting results from each sample set; production of a color poster to depict examples of elemental patterns along with regional geological information; production of this explanatory document; and publication of all materials on the MGS web site.

## **REGIONAL GEOLOGY**

The Quaternary geology of Minnesota (Hobbs and Goebel, 1982) is, at the land surface, dominated by till related to Late Wisconsinan glaciation. In the central and northeastern regions of the state, the till is sandy, and sand and gravel deposits are common. In the west and south, the till is silty with numerous carbonate clasts. Older tills occur in the subsurface and at the surface in the southwest and southeast parts of Minnesota. Sand and gravel are extensive in the central part of the State, and silty clay deposits of Lake Agassiz dominate the far northwest. The Late Wisconsinan tills are readily divisible into three distinct subgroups (Figure 1): the carbonate and shale-bearing sediments of the Des Moines lobe and its sublobes that were derived from the Red River valley/Lake Winnipeg region; the red-volcanic-rock-bearing sediments derived from the Lake Superior basin and deposited by the Superior lobe; and intervening sediments of the Rainy lobe that were derived from the northeast and that are dominated by debris such as granite clasts. The Rainy lobe split as it diverged around the bedrock high of the Mesabi Iron Range, resulting in the Wadena lobe to the north, which deposited sediment in west-central Minnesota that was moderately rich in reworked carbonate, and the Brainerd lobe to the south, which deposited carbonate-poor sediment in east-central Minnesota. Beyond the limit of Late Wisconsinan glaciation in the southeastern and southwestern corners of the state, are the older tills that were derived from northwest sources, and bear a moderate level of carbonate and a lower level of shale than the Des Moines lobe tills.

Minnesota bedrock geology (Morey and Meints, 2000) ranges from thin and discontinuous Mesozoic sedimentary rocks primarily in the southwest, to Paleozoic carbonates and sandstones in the southeast and the far northwest, to a diverse array of Precambrian rocks that comprise the bedrock surface from parts of southwestern Minnesota to the entire northern portion of the state. The youngest of these Precambrian rocks include Mesoproterozoic sandstones extending southwest from Lake Superior, as well as volcanic rocks and Duluth Complex gabbros and associated rocks along the north shore of Lake Superior. Paleoproterozoic rocks include the Sioux Quartzite of the southwest, and a broad array of rocks in central Minnesota, including the widely-mined iron-formation of the Mesabi Iron Range. The oldest rocks exposed at the bedrock surface, of Archean age, occupy roughly the northwestern third of the state, and consist of greenstone belts and intervening intrusions and metamorphic rocks ranging in grade up to gneiss and migmatite.

## **FIELD AND LABORATORY METHODS**

The soil data were obtained as part of a USGS national geochemical survey of stream sediments and soils. Across the U.S., stream sediments were favored for the USGS survey as a way to obtain insights into an entire drainage basin, but if specifications regarding drainage basin development such as lack of lakes could not be met within a given grid cell, soil samples at two discrete horizons were obtained. The majority of samples in Minnesota were from soil. Stream sediments were mostly collected in 1979, mainly from west-central and western Minnesota as part of the National Uranium Resource Evaluation program. Subsamples had remained in storage at the USGS and were reanalyzed in 2005. New samples for Minnesota were collected by staff of MGS in 2004 and 2005, at a spacing of 16 km, following USGS protocols (Figures 2 and 3). One-quarter of each 16-km grid cell was randomly chosen for the sample site. From those sites about 10 percent were randomly selected to have additional samples collected for analysis of variance (AOV). All grid sample locations were pre-selected and plotted on 1:250,000 scale quadrangle maps prior to the start of field work. This new soil and stream sediment sampling was completed by MGS, on contract to the USGS. Soils were sampled from shovel holes at sites away from human disturbance, first from the top 0.2 meter, and then from about 0.5 meter depth. A list of the elements analyzed and the lower limits of detection are provided in a digital file. The AOV data were not included in the atlas maps, but are provided as a separate data table. Analyses used USGS method ICP-40, consisting of near-total acid dissolution followed by ICP-AES, on sediment sieved to <150 $\mu$ . The elements mercury, arsenic, and selenium were analyzed by hydride-generation atomic absorption. The elements gold, platinum, and palladium were analyzed by fire assay of 30g of prepared material followed by atomic absorption spectroscopy (AAS). Additional information on the sampling and analytical method, elements analyzed, and detection limits is available on the USGS National Geochemical Survey web site. A total of 522 soil sites have data from the top 0.2 meter and 524 from about 0.5 meter depth. Stream sediment results total 306 samples. The two soil samples were averaged at each site and plotted along with the stream sediment results, which also were averaged if a duplicate value was present. Thus the plots show 524 soil sites and 306 stream sediment sites for 830 site locations, but the database table lists 1,352 total samples. Analytical results reported as less than the detection limit were set to one-half of the detection limit. The Excel tables that are part of the open-file report retain the original data with unchanged detection limits.



Sampling of soil parent materials was conducted by MGS in 2004, as part of a cooperative project with industry, where the goal was to sample C-horizon tills across Minnesota (Figures 4 and 5). The primary purpose of the survey was to search for indicator minerals indicative of mineral deposits. However, a major secondary goal was to systematically map regional trends in till geochemistry. Till was chosen as the sampling medium due to its widespread extent, and a simpler history of derivation relative to sorted sediments such as gravel, sand, silt, or clay, and a single medium also facilitated interpretation. Two hundred and fifty samples of C-horizon till were collected by MGS geologists. Samples were collected at a 30-km spacing within grid cells designated at quarter-degree latitude and half-degree longitude spacing, covering Minnesota and immediately adjacent regions. At an arbitrarily chosen site within each grid cell, a shovel was used to excavate to apparently undisturbed sediment in a ditch or road cut. Sampling from between 1 and 2 m depth, a 15 liter plastic pail was filled with till, covered and sealed. At a few sites with more than one till, vertical profiles were also collected. Following Geological Survey of Canada protocols, subsamples were screened at  $<63\mu$ , and submitted to ALS Chemex for analysis following four-acid, HF-HNO<sub>3</sub>-HClO<sub>4</sub>-HCl, digestion. Only the most resistant minerals, such as zircon, are incompletely dissolved using this procedure. A list of the elements analyzed and the lower limits of detection are provided by Thorleifson et al. (2007). The ALS Chemex ME-MS61 ultra-trace method was used, which includes both inductively coupled plasma (ICP) atomic emission spectrophotometry (ICP-AES) and ICP-MS (mass spectroscopy), and provides concentrations for 47 elements. In addition, about 30 grams of the prepared material was analyzed by fire assay and ICP using ALS Chemex procedure PGM-ICP23 for platinum, palladium and gold by fire assay and ICP. Analytical results that were less than the detection limits for this dataset were set a one-half the detection limit. Along with additional results from the indicator mineral survey, the geochemical data was previously published as part of an earlier report by the MGS (Thorleifson et al., 2007). Element maps in this previous report were designed to focus on high outliers.

The ground-water chemical data presented here were produced as part of the MPCA ambient Ground Water Monitoring and Assessment Program (GWMAP), a baseline study of water quality in Minnesota aquifers commonly utilized for domestic water supply (Adolphson et. al., 1981; Figures 6 and 7). For this survey, a randomized grid design was established across the state, with a grid node spacing of 11 miles. A well from each identified aquifer used as a source of drinking water was selected within a nine-square-mile target centered on each grid node. Between 1992 and 1996, 954 drinking water wells were sampled in this manner. Field measurements were made for pH, oxidation-reduction potential, dissolved oxygen, temperature, alkalinity, and specific conductivity. The samples were analyzed using ICP-MS following EPA protocols and other methods, by labs at the University of Wisconsin, and the University of Minnesota. Included in the analyses are major cations and anions, trace inorganic constituents, volatile organic compounds (VOCs), total organic carbon, tritium, as well as total suspended and dissolved solids. Mean, median, minimum, maximum, 95th percentile, and 95th upper confidence limit concentrations were determined for all inorganic parameters for thirty individual aquifers, seven age-based aquifer groups, and four hydrology-based aquifer groups. Effects of well diameter, sampling year and month, presence or absence of VOCs or tritium, well depth, static water elevation, geographic location, and redox parameters such as dissolved oxygen, total iron and manganese concentrations, and oxidation-reduction potential on concentrations of each chemical parameter were determined for all aquifers and aquifer

groups. Concentrations were compared with drinking water criteria and a risk analysis was completed (MPCA, 1998). For the current compilation, duplicates and multiples were removed from the plotted data. VOC analyses are provided in a table but were not included with the geochemical plots. Analytical results that were less than the detection limits for this dataset were assigned a value of half the detection limit. The list of the elements analyzed and the lower limits of detection are provided in an accompanying digital file. Additional information along with MPCA final reports and interpretations can be obtained from the MPCA web site.

## **RESULTS**

Results from this data compilation are provided as an MGS Open-File Report. The Open File includes this document, atlas maps for each variable, a poster, and digital data files, all of which are available on the MGS web site. For the atlas pages, symbol classes were based on groupings calculated by the ESRI ArcMap software using the natural breaks method. Five class boundaries were established for each map where relatively large jumps occurred in the data values. The Geochemical Landscape of Minnesota poster includes an example of the atlas map pages, five selected maps for each of the sample media, short explanations for each, and at the top of the poster, six maps showing Minnesota topography, depth to bedrock, bedrock outcrop localities, glacial sediment provenance, and generalized surficial and bedrock geology maps. An ESRI geodatabase is provided that contains the map data as plotted. In addition, Excel tables are provided for each data set including the upper and lower soil data, stream sediment data, soil AOV data, till data, and original MPCA ground-water data. All of the data tables include location coordinates for each sample. There is also a 'readme' file explaining the listing of tables.

The atlas maps indicate varying elemental patterns that occur in soil, till, and sampled ground water across Minnesota. Differences between the stream sediments sampled in the west and soil that was sampled in the east are apparent for some elements. Calcium, for example, appears to be depleted in the soils, presumably by dissolution of calcite, while the stream sediments seem to include freshly eroded, calcite-bearing sediments. For many elements in the soil data, however, no discernible difference between stream sediments and soil is apparent. Several patterns in the soil and soil parent materials correlate to glacial sediment provenance in relation to known glacial lobes such as the Des Moines lobe and Superior lobe, or in some cases in relation to sorted sediments such as sand or clay. Some elements show a correlation with sediments derived by glacial sediment transport from distinctive rocks such as gabbro in the northeast, while others are elevated in the west, in areas of shale-bearing glacial sediments. The elemental patterns in the till may partially explain patterns in overlying soils, although soil chemistry would be expected to have more complexity due to the presence of sorted sediments as parent materials, along with physical, chemical and biological processes of soil development, and possible contamination. The ground-water chemistry maps, as previously indicated by MPCA, show that some regional patterns can be discerned, at least for the time period during which the sampling was completed, despite sampling from multiple aquifers differing significantly in depth and geology. Some elements in the ground water show similar patterns to those in the soil or till, although others do not, which is not surprising given that most well water samples were derived from depths well below the soil, with different geologic contexts associated with the multiple aquifers that were sampled.

This data thus are meant to serve as a reference for persons engaged in interpretation of geochemistry, including use of the data to clarify regional context as a reference for more detailed surveys. Users are urged to be aware that information supplementary to the atlas pages will be required for their analysis, particularly in the case of the well water derived from aquifers of greatly varying depth and geology. Indications of well water sample depth and geology are provided in the data tables for example. In addition, users are referred to much more detailed data available from various agencies for portions of the state.

## **ACKNOWLEDGMENTS**

Thanks to Christopher Gonzales at MGS for assistance with data processing. We would like to acknowledge the role of Dr. Andrew Grosz of the U.S. Geological Survey, along with members of the National Geochemical Survey project, in the design and implementation of the soil and steam sediment survey in Minnesota. Similarly, the role played by WMC Resources Ltd. in completion of the till survey is acknowledged with appreciation. In addition, a strongly supportive partnership with the Minnesota Pollution Control Agency, in particular with Dr. Mindy Erickson, now of USGS, is very much appreciated. The Minnesota Minerals Coordinating Committee is recognized for the support that enabled compilation of these survey results.

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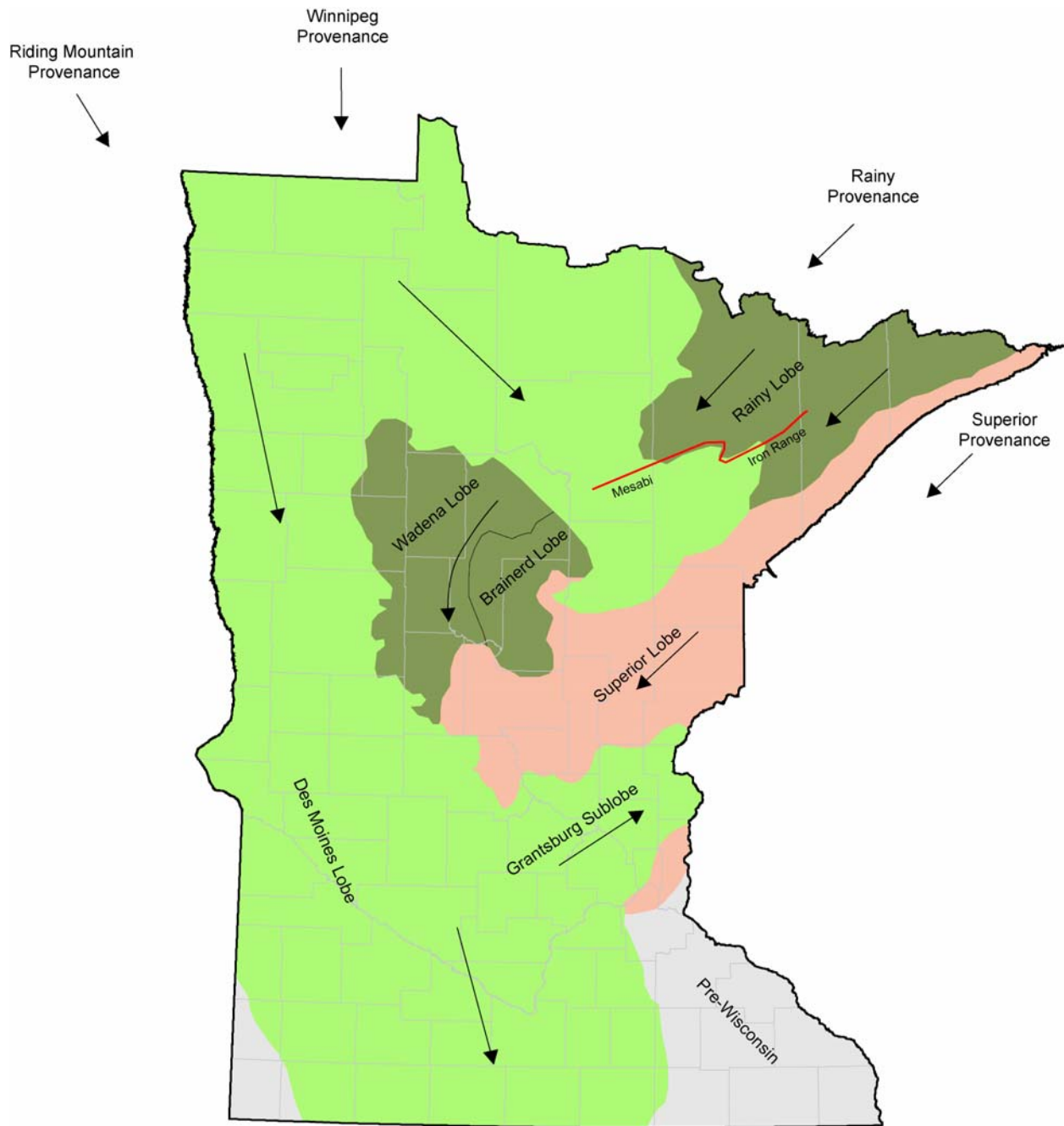


Figure 1. Direction of ice flow and provenance of glacial sediments in Minnesota.



Figure 2. Typical soil sampling conditions.

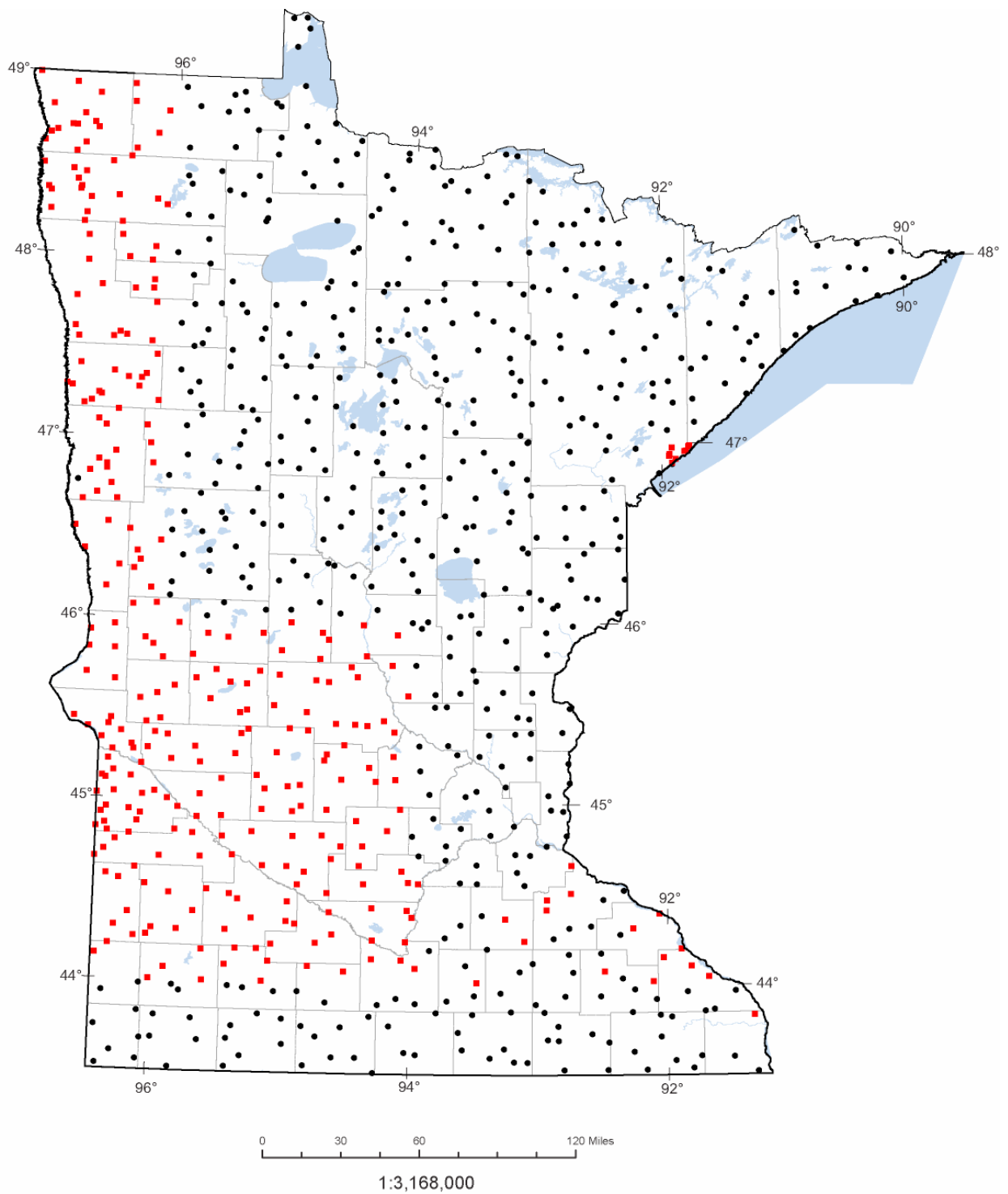


Figure 3. Location of soil (black circles) and stream sediment (red squares) sites.



Figure 4. Typical till sampling conditions.

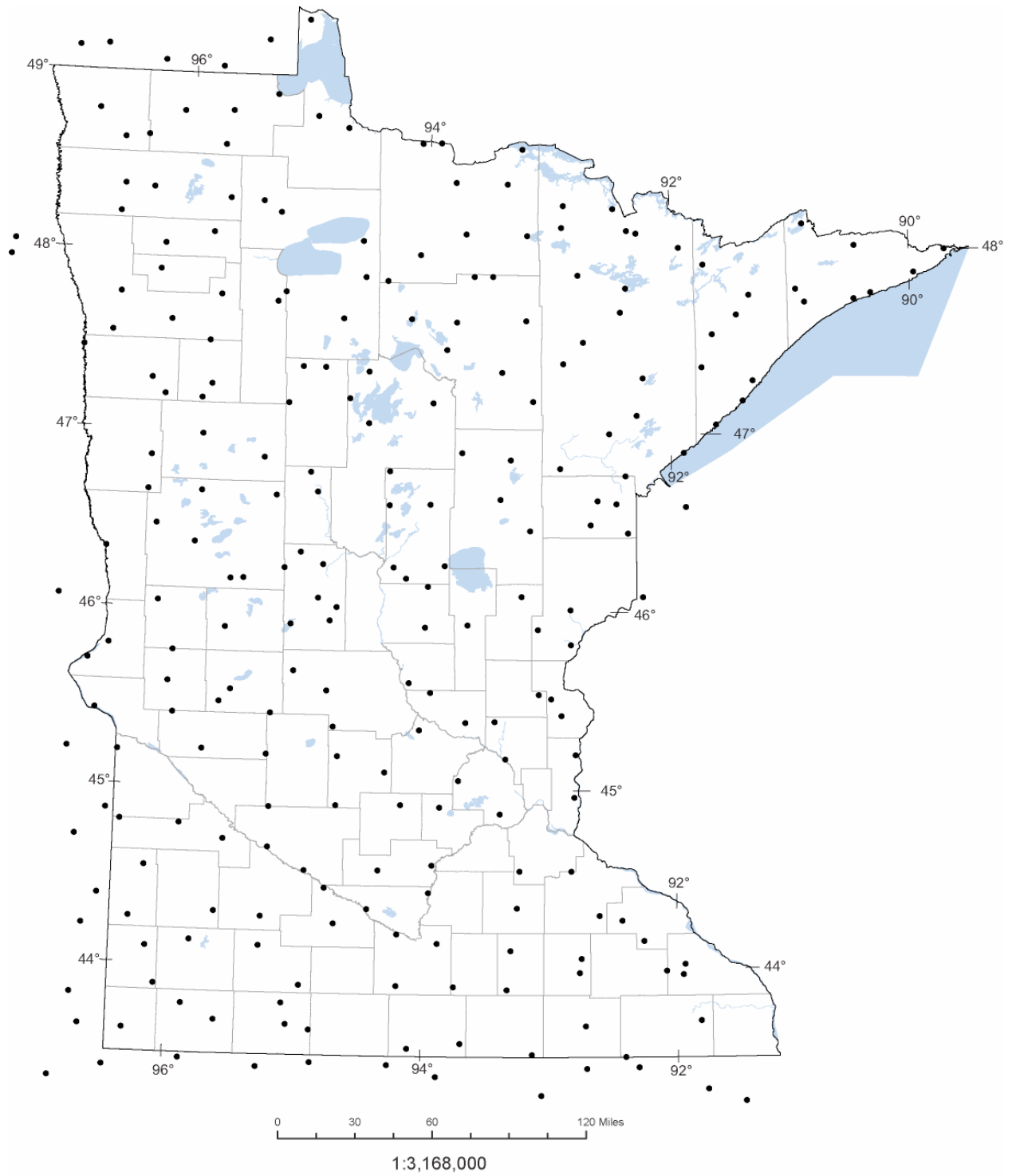


Figure 5. Location of till sample sites.



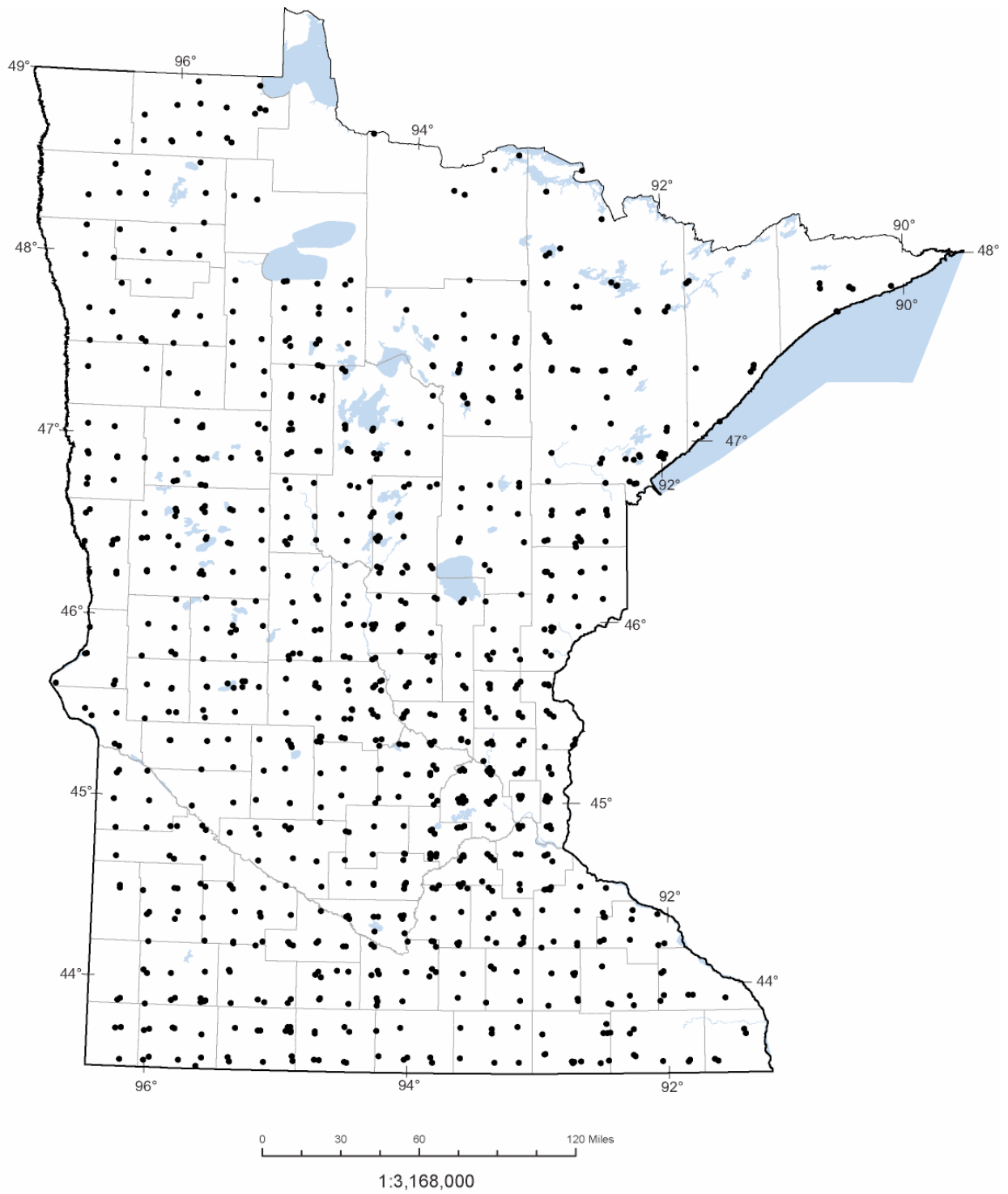


Figure 6. Location of well water sampling sites.

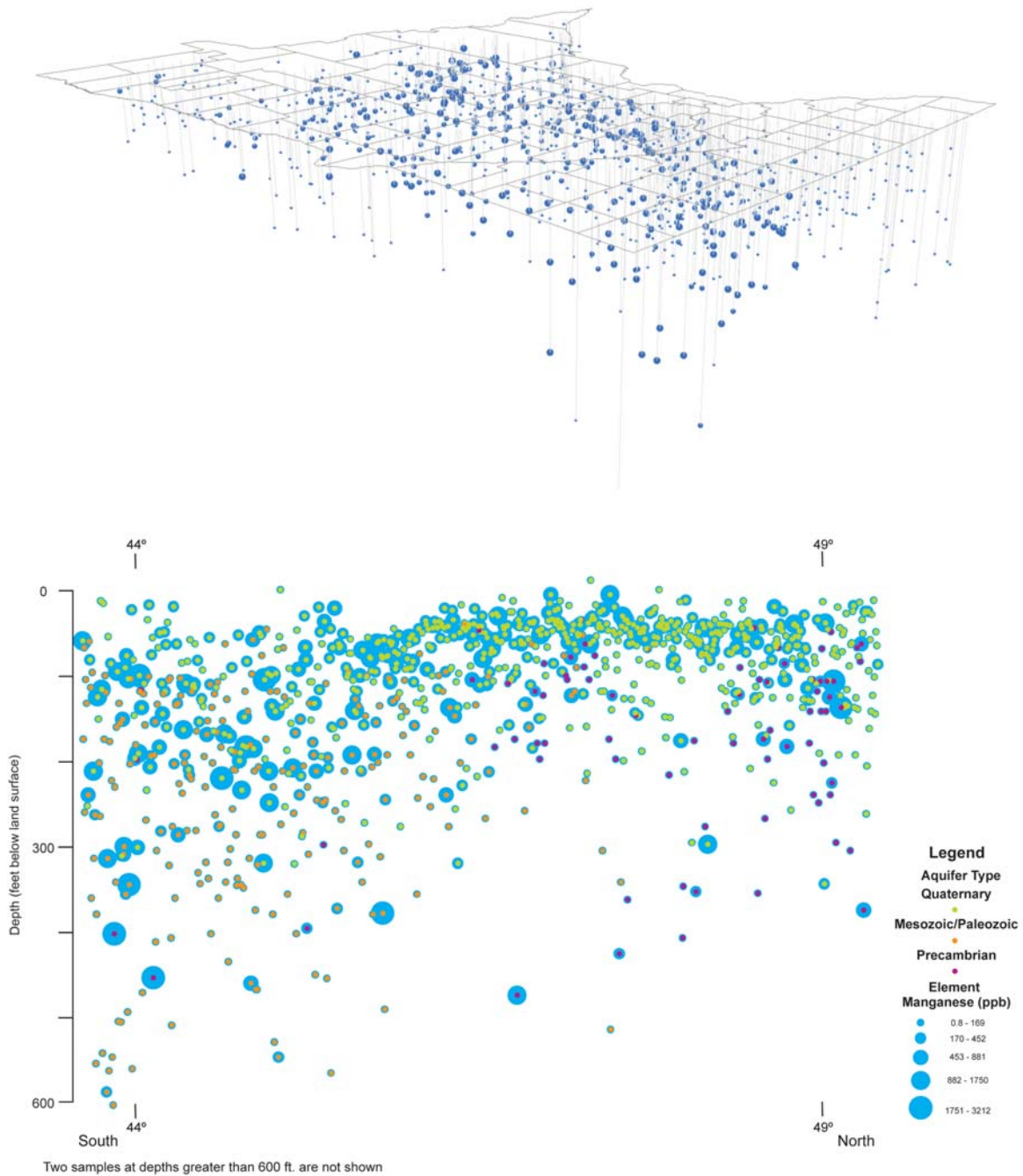


Figure 7. Two depictions indicating the 3D nature and varying geologic context of the well water data, using manganese as an example. The upper figure is a 3D oblique statewide view looking from the southwest; the lower figure shows all data projected onto a south to north section view