

Ionic Content Analysis of Groundwater in Rice, Dakota and Goodhue Counties

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Introduction

Southeastern Minnesota bedrock is composed mostly of Ordovician and Devonian sedimentary rocks of the Paleozoic period (Figure 1). Stratigraphy columns of the Rice County region show layers of dolostone, limestone, sandstone, and shale (Figure 2). Sandstone is a rock with high porosity and permeability, making it good material for the development of aquifers. Limestone is conducive to the formation of karst topography, which includes formation of caves and the development of aquifers as acidic rain and groundwater dissolve calcium carbonate rocks to form pores. The bedrock geology of the region indicates that aquifer layers lie relatively close to the surface, although they are carpeted by a thick layer of glacial till in most locations (MN Geological Survey (MGS), Caves in MN). Figure 2 also shows a bowl-shaped structure common to the stratigraphy of South-Eastern Minnesota that is effective at collecting groundwater as it percolates to the area of lowest elevation at the center of the bowl. This system is very different from the stratigraphy of Northern Minnesota, where layers of fractured igneous and metamorphic rocks leftover from the Keewanan rifting system have built an aquitard layer over the Paleozoic carbonate rocks (MGS, Caves in MN). The relative lack of overlying aquitards in the area makes it a good study area for groundwater analysis.

Aquifers are found in several layers beneath Southeastern Minnesota, including the St. Peter Sandstone, the Prairie du Chien Group (dolostone), and the Jordan Sandstone (MGS, Caves in MN). The St. Peter-Prairie du Chien-Jordan formation is a major aquifer underlying most of southeastern Minnesota including Rice County (Ruhl et. al. 2002). This aquifer is a source of drinking and irrigation water for most farmers in the

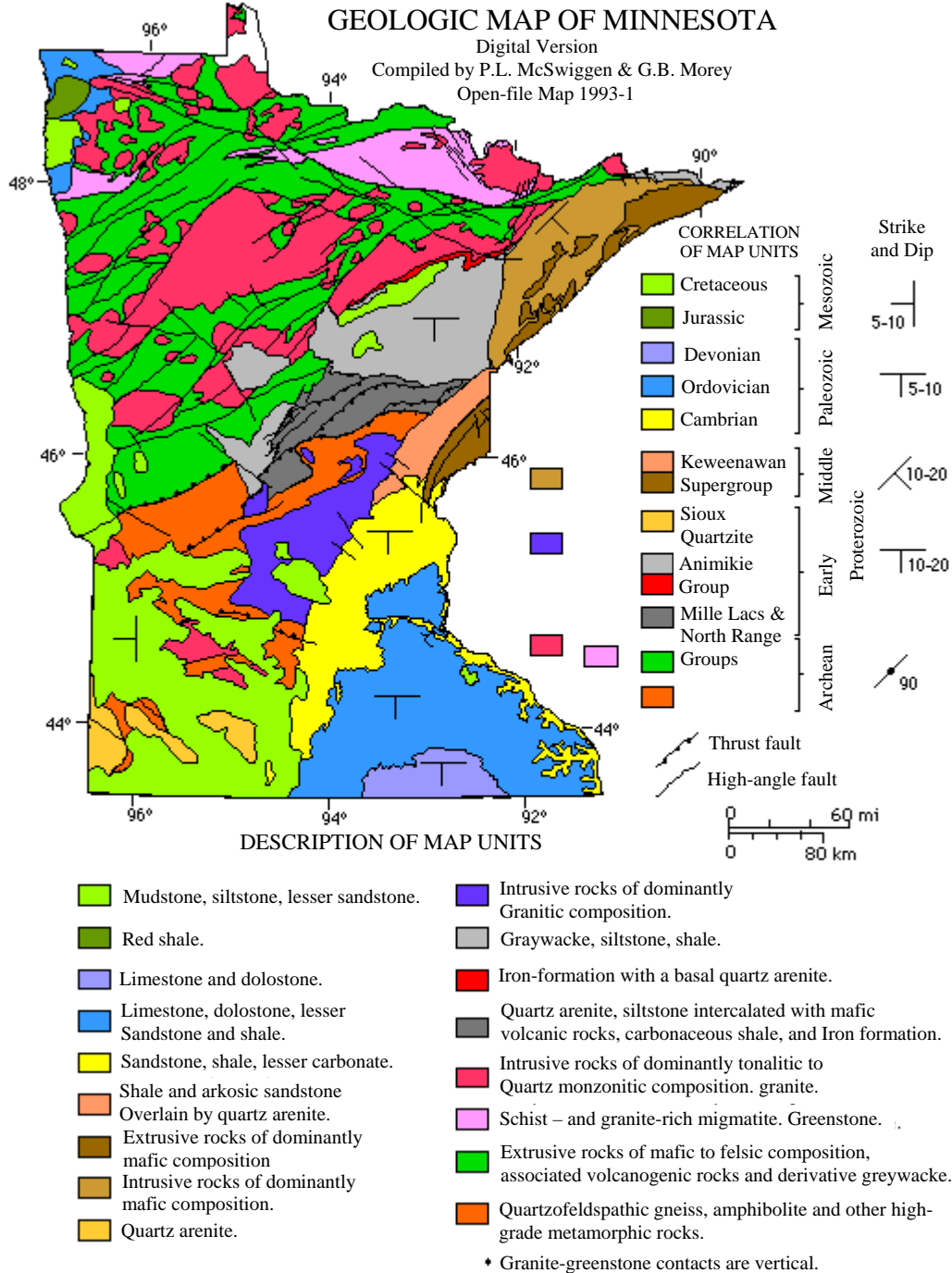


Figure 1. Bedrock map of Minnesota. Southeastern Minnesota is composed principally of Devonian, Ordovician, and Cambrian rocks. These relatively young rocks are principally sandstones and carbonate limestones. (Source: <http://www-users.cs.umn.edu/~checheln/geo/images/bdrkmod.gif>)

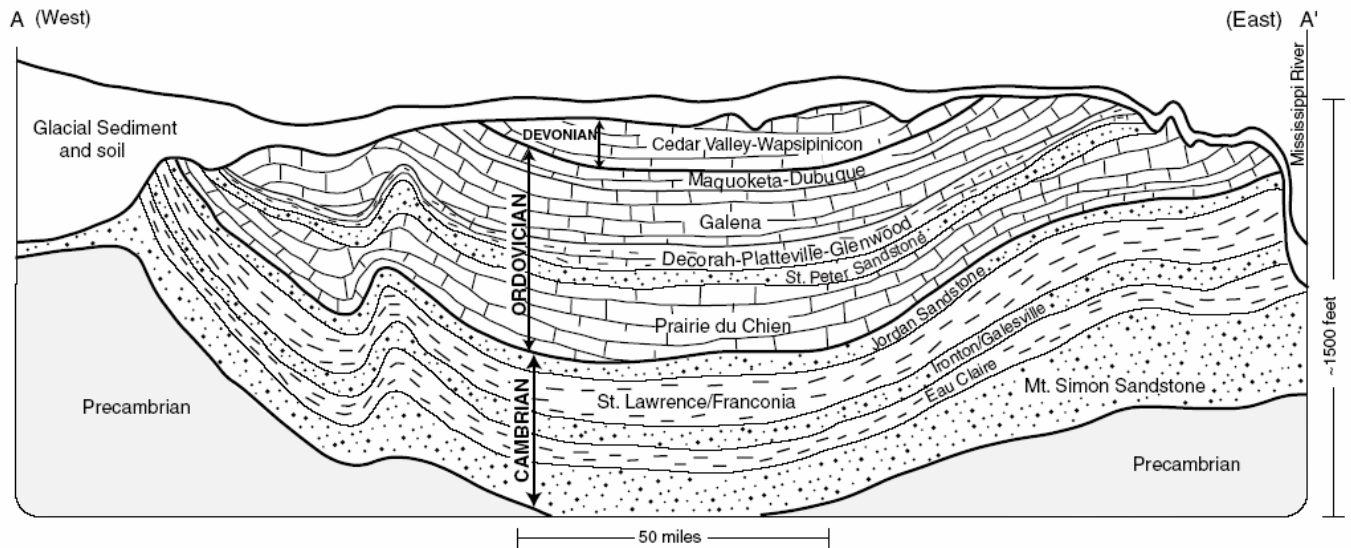


Figure 2. Stratigraphy diagram of underlying rocks in the Southeastern Minnesota region. A layer of glacial sediment and soil overlies layers. These layers form a bowl shape that efficiently channels water in aquifers to the center of the region, providing a ready and quickly renewing source of water for the region. (Source: Minnesota Geological Survey, Ancient Tropical Seas)

region. Figure 3 shows three Minnesota counties that lie over these aquifers (Rice, Goodhue and Dakota Counties); these are the three counties focused on by this study.

Due to the highly porous karst topography, groundwater is easily affected by surface runoff. In an area of intense farming such as Rice County pesticide and fertilizer runoff can quickly contaminate aquifers. Groundwater supplies 75 percent of Minnesota's drinking water so it is important to monitor levels of potentially dangerous ions in groundwater (MN Department of Natural Resources). In early 2004 undergraduates from Carleton College conducted extensive testing of 19 local wells and springs. While the Carleton Winter 2004 Study focused on testing both ionic content and age of groundwater, this Carleton Fall 2004 Study focuses mainly on the ionic make-up of groundwater. The purpose of this study is to follow up the Carleton Winter 2004 Study by testing new samples for the same ions that the Carleton Winter 2004 Study researched, and to compare and contrast previous results with more recent findings. To

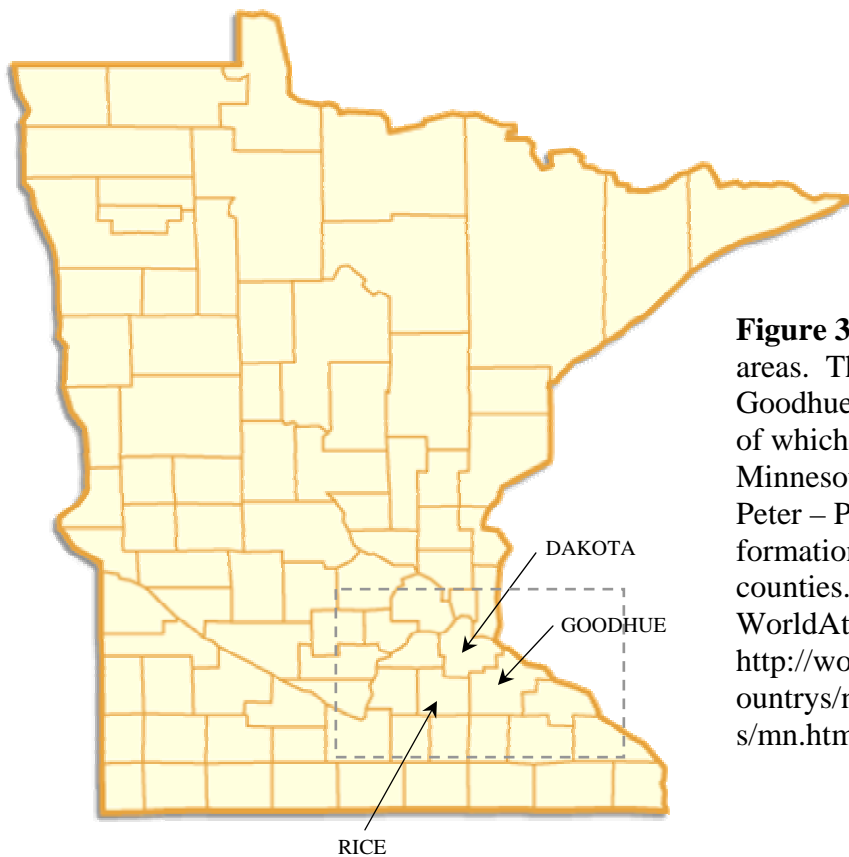


Figure 3. Map of principle study areas. This study focuses on Rice, Goodhue, and Dakota counties, all of which lie in Southeastern Minnesota. Aquifers of the St. Peter – Prairie du Chien – Jordan formations lie beneath these counties. (Outline Map from WorldAtlas.com, <http://worldatlas.com/webimage/countrys/namerica/usstates/counties/mn.htm>)

conduct this study, 5 samples were collected from wells owned by farmers in Rice, Dakota and Goodhue Counties, and one sample was collected from the Carleton College well located in the facilities steam plant. Four unanalyzed samples from the Carleton 2004 Study collected from wells in the greater Northfield area were also analyzed.

Methodology

A total of 10 water samples were collected from wells around Rice, Dakota, and Goodhue counties in South-Eastern Minnesota. Four of these samples were collected by the Carleton Winter 2004 Study within a week in late January and early February 2004. Samples of the Winter 2004 Study were collected in 4 oz. SKS glass bottles and filled while submerged to prevent air contamination. For the Carleton Fall 2004 Study, one sample was collected directly from the Carleton College well in early October. The

remaining 5 samples for the Carleton Fall 2004 Study were collected over a period of 2 weeks in mid-October 2004. Four ounce SKS glass bottles with foil-lined caps were given to farm owners in the greater Northfield area, who filled the bottles with water drawn directly from their farm wells.

At Carleton College, samples were run through an Atomic Absorption Spectrometer to test for calcium and mercury. Concentrations in mg/L were obtained by first constructing a calibration plot with dilutions of a known standard, and then running the samples. A Dionex Ion Chromatograph was used to perform anion analysis. The water samples were tested for F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} . Using an auto-injector, a 5mL vial was filled for each sample, loaded into the IC, and then analyzed for anion content.

Discussion of Previous Works

Previous research on dissolved ions in Minnesota groundwater has been conducted by both Carleton College and the USGS.

Regarding anions, the Carleton Winter 2004 Study found no amount of bromide and phosphate in any of their samples. Sulfate and chloride were always present, often in large amounts, with concentrations ranging from 0.11 to 62.93 mg/L and 0.08 to 72.54 mg/L, respectively. Fluoride was always present as well, but in smaller concentrations, which ranged from 0.14 to 0.32 mg/L. Nitrate-N was found in 14 of the 19 Winter 2004 study samples, with concentrations ranging from 0-13.52 mg/L. Nitrite-N was detected in only three of the test sites, with concentration levels ranging from 0.14 to 0.83 mg/L. Regarding cations, ammonium was only found in two wells, and the values were 2.06 and 0.27 mg/L. Lithium levels were extremely low, with a maximum concentration of 0.65

mg/L. Sodium levels ranged from 5.42-45.31 mg/L, with most samples falling under 25 mg/L. Potassium levels were relatively low across the board, ranging from 0.97-7.50 mg/L with one well showing a potassium value of 89.62 mg/L. Magnesium concentrations varied from 28.94-63.14 mg/L. Calcium levels were a bit higher overall, ranging from 39.08-109.03 mg/L. Conclusively, major ion concentrations measured by the Carleton Winter 2004 Study indicated a likely anthropogenic input of chloride and more importantly nitrate in shallow wells, while ions like potassium and ammonium were found in very small amounts, and bromide, phosphate, and nitrite were practically non-existent (James et. Al, 2004).

The USGS has previously tested for mercury, an incredibly toxic chemical that can be found quite readily in very small doses in nature. The maximum level of mercury contamination considered safe by the EPA is 2 ppb (EPA). Frequently occurring sources of mercury in Minnesota include industrial wastes, sewage sludge, mining wastes and fossil fuel combustion, all of which are man-made and often improperly shielded from water sources (DNR, Geologic Atlas).

Results

Of the seven anions for which we tested using the Dionex Ion Chromatograph, no samples contained bromide, or phosphate. Only one of the samples contained nitrate, with a concentration of 4.79 mg/L, and only one of the samples contained nitrite with a concentration of .1400 mg/L. Seven samples contained fluoride, with amounts ranging from 0.05 to 0.20 mg/L. All of the samples contained chloride and sulfate, often in significant quantities, with sulfate ranging from 8.72 to 45.01 mg/L, and chloride ranging from 0.69 to 20.43 mg/L. In all but one of the samples, the sulfate content was higher

than that of chloride. Calcium was present in all of the samples, with concentrations ranging from 21-29 mg/L in the Fall 2004 Study samples as detected by the Atomic Absorption Spectrometer. While standards were prepared for Mercury calibration by the Atomic Absorption Spectrometer, a successful calibration curve was not attained, and therefore mercury content in the samples could not be analyzed.

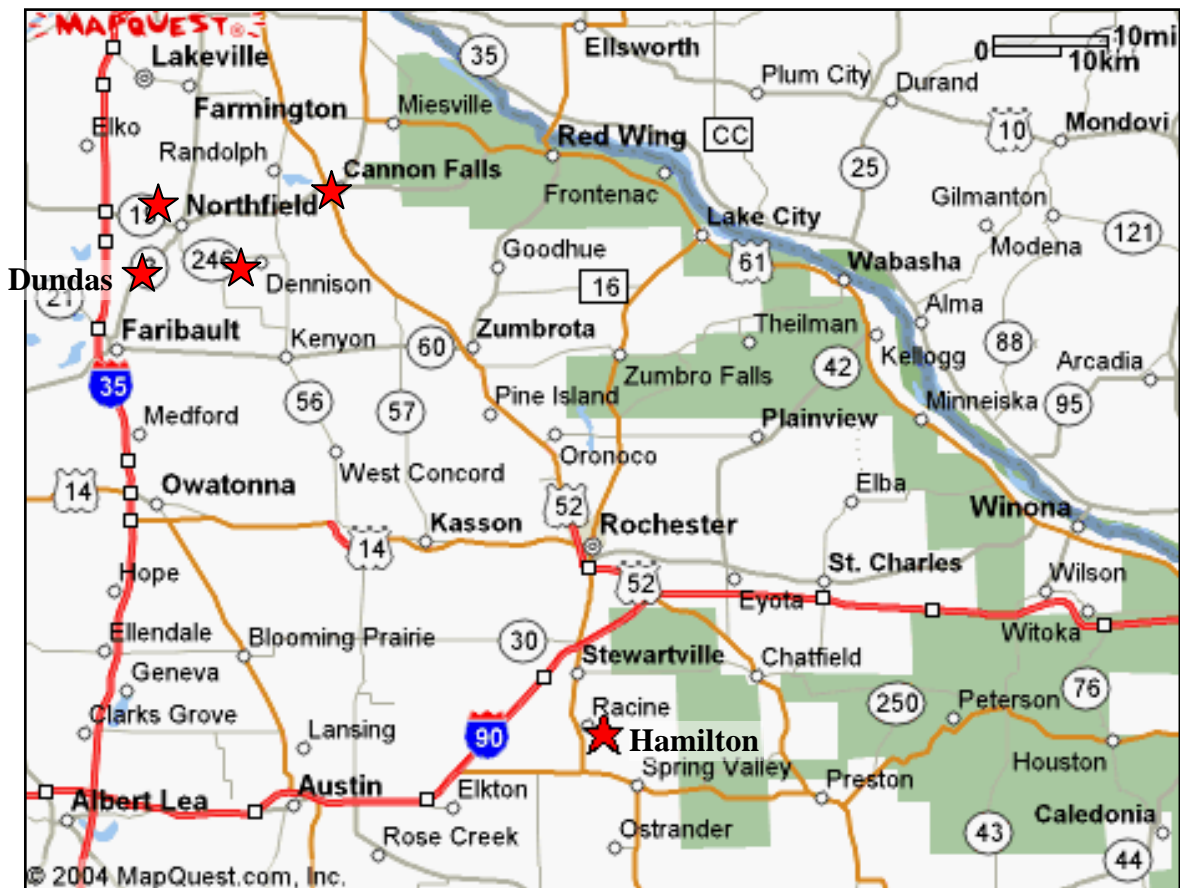


Figure 4. Map of sample collection sites. Most samples were collected in the greater Northfield area, with one sample collected farther to the southwest in Hamilton, Goodhue County.

Table 1. Levels of Calcium in groundwater samples from Rice, Goodhue, and Dakota counties, South-Eastern Minnesota. Only samples collected in fall 2004 are shown here due to equipment problems with cation analysis for the remaining samples.

Sample #	Ca ²⁺
1 (Dundas)	27
2 (Cannon Falls)	22
3 (Northfield)	21
4 (Dennison)	21
5 (Hamilton)	29
6 (Carleton)	21

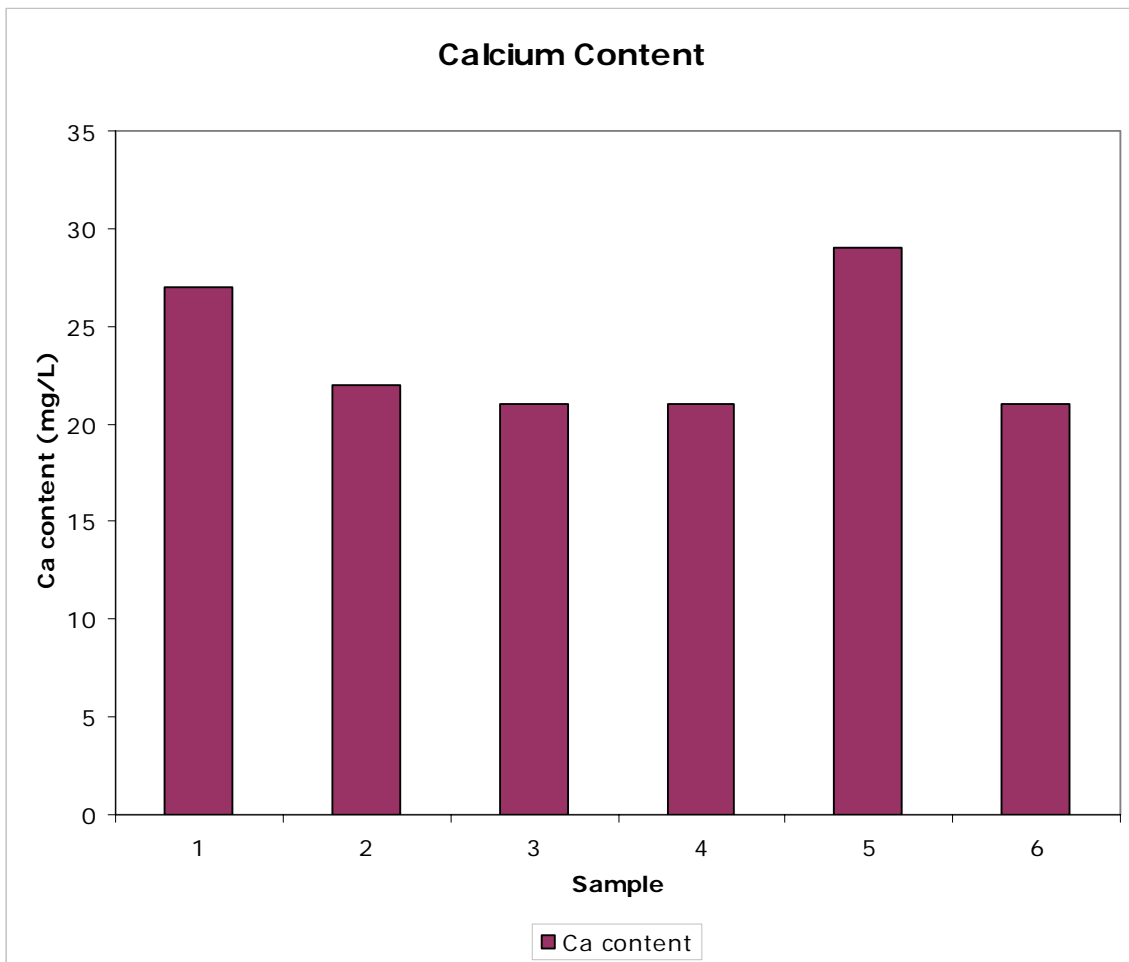


Figure 5. A comparison of calcium concentrations in water samples collected from Rice, Goodhue, and Dakota county. Concentration levels are fairly similar between sites but overall, calcium is found in much higher concentrations than any other ion tested for with the possible exception of sulfate.

Table 2. Concentrations (mg/L) of 7 anions in groundwater samples from Rice, Goodhue, and Dakota counties. The first six samples are those collected by the fall 2004 group. The remaining 4 samples are those collected by the winter 2004 group. These 4 are identified by the name of the well-owner; the general locations of the wells were not mentioned by the winter 2004 group.

Sample #	Fl ⁻	Cl ⁻	Br ⁻	NO ₂ ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
1 (Dundas)	0.00	1.01	0.00	0.00	0.00	0.00	12.44
2 (Cannon Falls)	0.00	2.99	0.00	0.00	4.79	0.00	45.01
3 (Northfield)	0.00	2.19	0.00	0.00	0.00	0.00	9.15
4 (Dennison)	0.14	0.69	0.00	0.00	0.00	0.00	39.48
5 (Hamilton)	0.05	20.43	0.00	0.00	0.00	0.00	14.13
6 (Carleton)	0.16	1.02	0.00	0.00	0.00	0.00	17.67
7 (Flatten)	0.19	1.13	0.00	0.14	0.00	0.00	8.72
8 (Braucher)	0.18	10.45	0.00	0.00	0.00	0.00	8.80
9 (Dobrahner)	0.19	1.10	0.00	0.00	0.00	0.00	38.70
10 (Frame Deep)	0.20	1.60	0.00	0.00	0.00	0.00	13.88

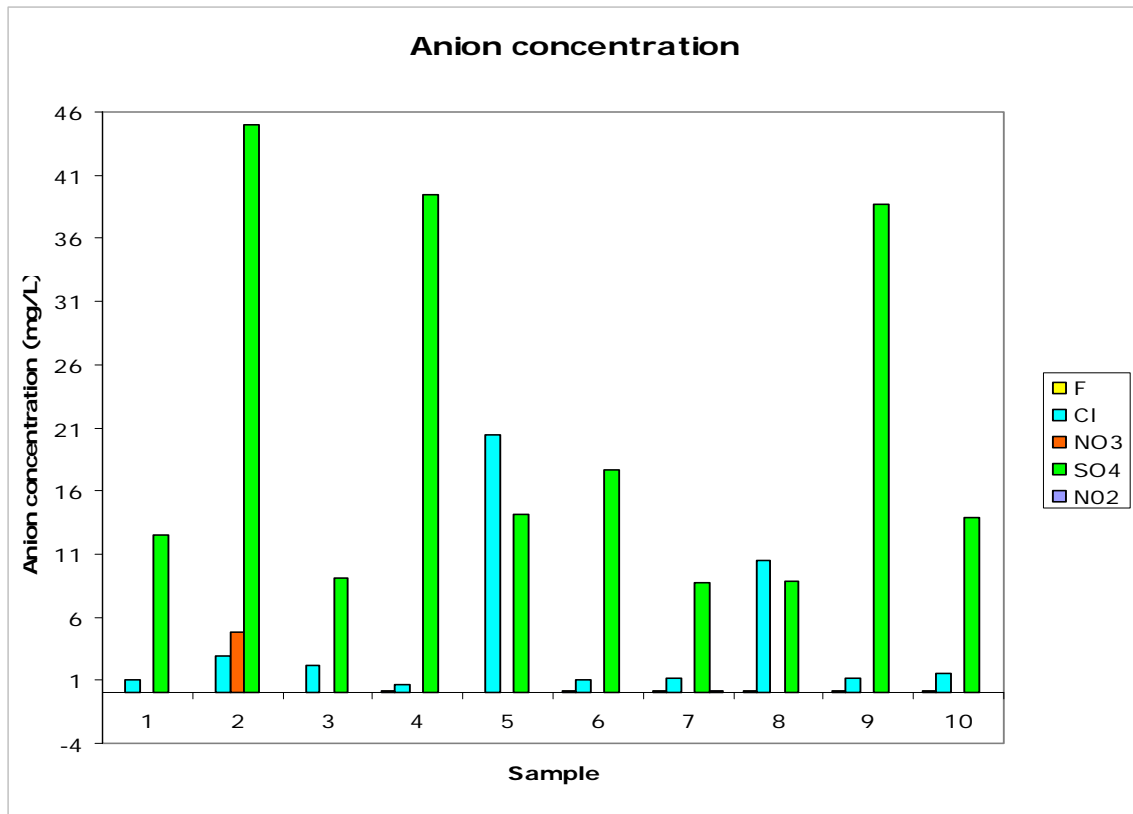


Figure 6. Graph of anion concentrations in all samples. Sulfate shows by far the greatest concentration in nearly all samples, while Nitrite and Fluoride are relatively scarce.

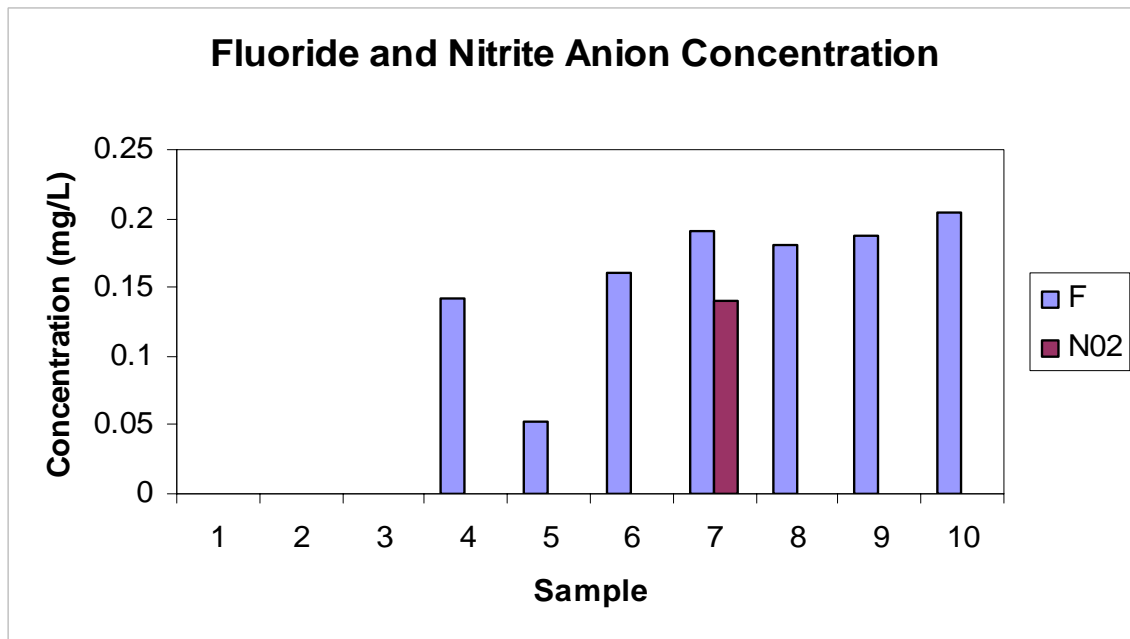


Figure 7. A closer look at Fluoride and Nitrite anion concentrations. As these concentrations were too small to be effectively shown in figure 6, an additional graph was made. Fluoride concentration values were relatively similar in all samples except for samples 1-3 and 5, where Fluoride was quite scarce.

Discussion

Chloride content in the samples, ranging from 0.69 to 20.43 mg/L, was not in violation of any EPA standards. Chloride, unlike many substances, does not have any regulations on its content in drinking water. However, the EPA advises that some people who use drinking water containing large amounts of chloride (250 mg/L and above) could experience irritation of the eyes and nose, and possible stomach discomfort (EPA). The primary natural source of chloride is halite in rocks. Anthropogenic sources include road salts, fertilizers, and waste material (MPCA, 1999a).

The fluoride content, with a range of 0.05 to 0.20 mg/L, was also in compliance with EPA standards. The EPA has set an enforceable drinking water standard for fluoride of 4 mg/L (some people who drink water containing fluoride above this level over many years may contract bone disease). The EPA has also set a secondary fluoride standard of 2 mg/L to protect against dental fluorosis. None of the analyzed samples came close to this level. However, at high fluoride concentrations, dental fluorosis, in its moderate or severe forms, may result in a brown staining and/or pitting of the permanent teeth. This problem occurs only in developing teeth, before they erupt from the gums. Children under nine should not drink water that has more than 2 mg/L of fluoride (EPA). The main source of fluoride in groundwater is the weathering of igneous rocks, although fluoride is also found in limestone and dolomite. Previous tests have concluded that there is little anthropogenic fluoride contribution.

The ion chromatographer produced a sulfate range from 8.72 to 45.01 mg/L. The EPA does not have any specific limit on the amount of sulfate in water, but excessive amounts can educe an unpleasant taste and can have diarrheic effects. Sulfate is naturally

occurring in gypsum and pyrite, and can therefore easily contribute to the ionic composition of groundwater. Anthropogenically, sulfate production comes mainly from fertilizer and biological waste.

The one sample containing nitrate had a nitrogen concentration of 1.08 mg/L, which was under the EPA's acceptable limit of 10 mg/L. In the short run, excessive levels of nitrate in drinking water can cause serious illness and sometimes death. The serious illness in infants, known as "Blue Baby" Syndrome, is due to the conversion of nitrate to nitrite by the body, which can interfere with the oxygen-carrying capacity of the child's blood. This can be an acute condition in which health deteriorates rapidly over a period of days. Symptoms include shortness of breath and blueness of the skin, hence the name (EPA). In the long term, nitrates and nitrites have the potential to cause the following effects from a lifetime exposure at levels above the recommended level of 10 mg/L: diuresis, increased starchy deposits and hemorrhaging of the spleen. Primary sources of organic nitrates include human sewage and livestock manure, especially from feedlots. The primary inorganic nitrates which may contaminate drinking water are potassium nitrate and ammonium nitrate both of which are widely used as fertilizers.

As nitrite was only found in one sample, and because the concentration of .14 mg/L is so small, like the Carleton Winter 2004 Study, this was attributed to a "microprobe origin" and no further analysis was conducted (James et Al, 2004).

Calcium content in the tested samples ranged from 21-29 mg/L. The EPA currently has no restrictions on calcium levels, and no major health problems are associated with it. Calcium is common in minerals and soils of the region, and especially in dolomite, which composes part of the Prairie du Chien/Jordan aquifer. Compared to

natural sources, anthropogenic production of calcium is very limited (MPCA, 1999b). It is important to acknowledge that all samples were taken prior to any water softening treatment and therefore levels of calcium in drinking water would be even lower than the results indicated.

Calibration of the Atomic Absorption Spectrometer for mercury was attempted by creating five standards of ultra-low concentration, as mercury is found in miniscule concentrations in Minnesota groundwater. Unfortunately, the machine failed to properly read all the standards and was thus unable to create a proper calibration curve, making any testing impossible. The following concentrations were used for the attempted calibration of mercury: 0.5 ppb, 1 ppb, 2.5 ppb, 5 ppb, and 10 ppb. The Atomic Absorption Spectrometer read the first two standards, but afterwards misread the subsequent standards and therefore failed to give accurate readings for any of the samples.

Conclusions

Due to time constraints and equipment malfunction the amount and scope of data collected was limited. It was our original goal to analyze all available samples for arsenic, mercury and the presence of a variety of cations and anions. Unfortunately we were only able to test for the seven basic anions and calcium content. In all tests for mercury, we were unable to create an accurate calibration curve on the Atomic Absorption Spectrometer. Results for cations from the Dionex Ion Chromatographer were unobtainable because of mechanical malfunctions that made calibration of the machine impossible.

On the whole, the results of the groundwater testing fall within the range of concentrations analyzed by the Winter 2004 Study. As with the Winter 2004 Study, the

Fall 2004 Study found no amounts of bromide and phosphate in groundwater samples, and miniscule amounts of nitrite. While the Winter 2004 Study found nitrate in fourteen of nineteen samples, however, the Fall 2004 Study found nitrate in only one of ten samples. As the Winter 2004 Study discovered by dating groundwater samples, higher levels of nitrate are indicative of younger wells (James et Al, 2004). Because the Fall 2004 Study samples generally contained less nitrate than the Winter 2004 Study samples, it can be hypothesized that the wells sampled for the Fall 2004 Study were of older age.

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