Characterization of groundwater from Rice County, MN using CFC dating, H and O isotope analysis and ion concentrations

Kristen James, Karla Knudson, Brandon Murphy, Travis Ruthenburg, Alexandra Schmitt, Kathryn Stalker and Bereket Haileab*

Geology Department, Carleton College, One North College Street, Northfield, Minnesota 55057, bhaileab@carleton.edu

Abstract

Over the past four years undergraduate students from Carleton College have compiled extensive surface water chemistry data for Rice County, Minnesota. However, there is limited information available on groundwater chemistry. To address this samples were collected from a total of 19 private wells and springs and studied for their major ions, isotopes, and dissolved CFC concentrations. The major ions measured were fluoride, chloride, nitrite, nitrate, phosphate, and sulfate. By determining the dissolved gas concentrations of chlorofluorocarbons (CFC-11, CFC-12 and CFC-113) the age of the water in the wells and springs was determined. The groundwater displays d18O ranging from 8.67 to 9.80 and dD ranging from 54.00 to 75.00, consistent with regional meteoric recharge. Recharge dates range from 1940 for waters from the Jordan Formation to 1970 for the Shakopee Formation, while shallow wells show recharge within the last 2-3 years. Major ion concentrations indicate a likely anthropogenic input of chloride and, more importantly, nitrate in the shallow wells. Bromide and phosphate were not detected, nitrite was rarely found, and sulfate, chloride, and fluoride were always detected. Nitrate concentrations show a direct correlation with the recharge dates, with many recently sourced wells showing nitrate concentrations above the EPA standard for drinking water.

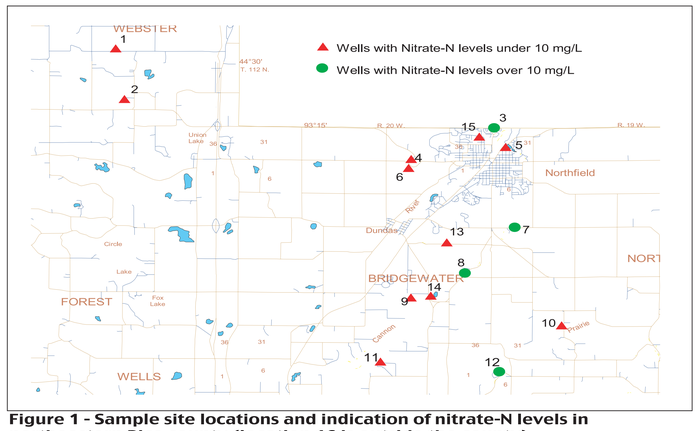

Figure 1 - Sample site locations and indication of nitrate-N levels in northeastern Rice county (location 16 is outside the county)

Nitrates-N

Nitrate-N values range from 0 to 13.52 mg/L with a mean level of 5.07 mg/L. Nitrate-N levels above 10 mg/L are alarming as this leads to health risks (MPCA, 1998). There are four wells in our study area where dangerous waters are located, (Figure 1). The Minnesota Department of Health has established a health risk limit of 10 mg/L for daily ingestion (MPCA, 1998). The major health danger of excess nitrates in drinking water is "blue baby syndrome" or methemoglobinemia, which occurs when bacteria in the stomach converts nitrate into nitrite, which reduces the blood's capacity to carry oxygen to vital organs (MPCA, 1998). Children and adults older than six months of age usually have enough stomach acid to inhibit methemoglobinemia-causing bacteria (MPCA, 1998). Further investigation of nitrate levels is warranted, especially correlating presence of nitrate with well depth; until then, local residents should be careful about well water consumption. The majority of the samples we obtained are located in what is assessed as a "very high" risk aquifer zone, where it can only take between hours and months of estimated vertical travel time before water-borne surface contamination could reach the aquifer (Campion, 1997). The main source of nitrates in water is anthropogenic, mostly from fertilizers, but also from improperly working septic systems (MPCA, 1998).

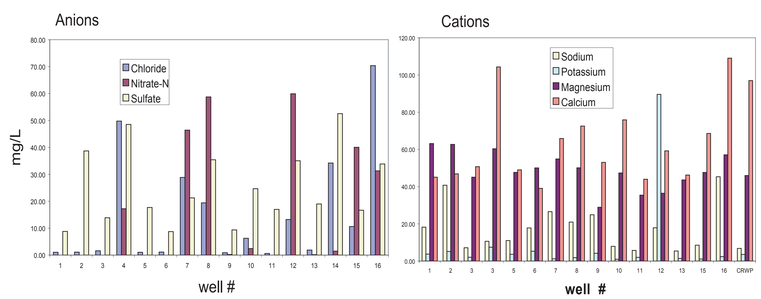

Figure 2 - Ion concentrations by well.

Sodium/ Chlorine comparison

The Rice County groundwater chloride data range from 0.08 mg/L to 72.54 mg/L. The primary source of chloride is halite in rocks, while the anthropogenic source is mainly road salt. The sodium values obtained ranged from 5.42 mg/L to 45.31 mg/L. The sodium values generally correlated with chloride, therefore indicating an anthropogenic input of both, most likely through road salting. Sodium is also commonly found in minerals and soil.

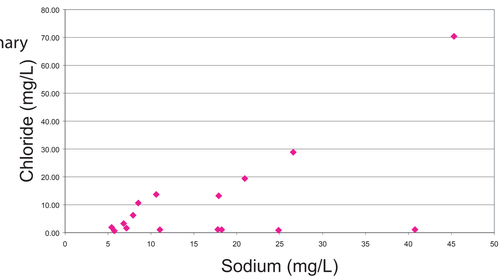

Figure 3 - Sodium concentration versus chloride concentration

CFC's

Using the estimated concentrations of CFC-11, CFC-12, and CFC-113 (Figure 2) as well as the Henry's Law solubilites of each species, the concentrations of each of the three CFCs can show the time since the water was isolated from the unsaturated zone (Busenburg and Plummer, 1992). See Table 1 for the calculated recharge dates based on each CFC species. For five of our wells, the calculated recharge dates from all three CFC species were comparable. Most likely, these dates are reliable indicators of how recently the water was recharged. For the rest of the wells, the dates did not agree. Possible reasons include: differences in sorption between the species, preferential microbial degradation, or VOC contamination.

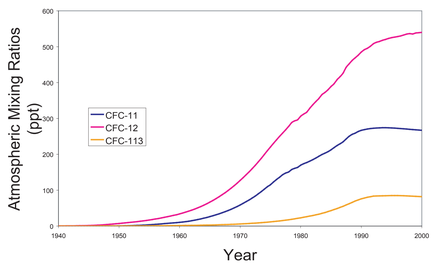

Figure 4 - Atmospheric CFC concentrations

Sample ID	CFC-11 recharge date	CFC-12 recharge date	CFC-113 recharge date
1	1967	1968	1940
2	1969	1967	1972
3	1973	1970	1974
3	1981	2004	1983
4	1975	2004	1979
5	1968	1963	1940
6	1981	2004	1984
7	2004	2004	1990
8	1991	2004	1989
9	1969	1969	1973
10	1985	1985	1986
11	1971	1968	1940
12	1986	2004	1978
13	1966	1961	1940
14	1967	1968	1940
15	1987	1989	1988
16	2004	2004	1988
CRWP	1969	1967	1974

Table 1 ñ Chlorofluorocarbon determined dates of water samples

Stable Isotopes

The groundwater displays 18O ranging from -8.67 to -9.80 and D ranging from -54.00 to -75.00, consistent with regional meteoric recharge. According to data compiled by Friedman (1964), d18O and dD values fall within the range for meteoric waters in this region of the country. These values agree with the relatively young apparent ages of the water and suggest a regional or local recharge area.

Sample ID	$\delta^{18}O$	δD
1.00	-8.33	-64.50
2.00	-8.53	-67.80
3.00	-8.67	-63.10
3.00	-9.46	-72.00
4.00	-	-70.70
5.00	-	-61.50
6.00	-	-56.40
7.00	-	-75.70
8.00	-	-66.00
9.00	-	-54.90
10.00	-9.70	-70.40
11.00	-	-75.70
12.00	-9.21	-61.00
13.00	-8.92	-57.00
15.00	-	-71.00
16.00	-	-66.20
CRWP Spring	-8.97	-66.70
CRWP Spring	-8.73	-

Table 2 ñ Stable oxygen and hydrogen isotope ratios relative to SMOW (parts per mil)

Conclusions

Oxygen and Hydrogen isotopic signatures and CFC content indicate that the surveyed Rice County wells are recharged from young meteoric sources. Wells recharged within the last 25 years show high nitrate levels, likely from anthropogenic sources. These levels excede Mnnesota depatment of Health recomendations for nitrate content in drinking water.

Future studies could be aided by a number of procedural modifications. The accuracy and precision of CFC dating can be improved by recording the water temperature during sample collection. Corroboration with the Tritium signature and SF6 content could prove useful for confirming the accuracy of CFC dating.

Acknowledgments

Funding for this project was provided by Carleton College Geology Department. We would like to thank Dr. Thure Cerling, Dr. D. Kip Solomon and Craig Cook for demonstrating and explaining the design of their instruments and methodology of CFC, Oxygen and Hydrogen Isotopes. The assistance of Dr. Francis Brown, Scott Hynek, Benjamin Passey, Melissa Klinder, Alan Rigby, is gratefully acknowledged. We are indebted to the following persons who have assisted in securing samples. Victor Suma, Claire Ericksen, David and Stephanie Henriksen, Jen Macalady and David Bice, Dobrahner, Cindy and Ed Buchwald, Gene Bakko, Jean and Lyale Myers, Jim Braucher, John and Vicky Tripp, John Dudley, John Maakestad, Lien, Mary Ellen Frame , and Robert Flatten.

References

Busenberg, E. P., L. Niel, 1992, Use of Chlorofluorocarbons (CCl3F and CCl2F2) as Hydrologic Tracers and Age-Dating Tools: The Alluvium and Terrace System of Central Oklahoma: Water Resources Research, v. 28, no. 9, p. 2257-2283.

Campion, M., 1997, Sensitivity to Pollution of the St. Peter- Praire Du Chien- Jordan and St. Lawrence- Franconia Aquifers." Geology Atlas of Rice County, Minnesota: St. Paul, Minnesota, Minnesota Department of Natural Resources.

Cook, P. G. H., Andrew L., 2000, Environmental Tracers in Subsurface Hydrology: Boston, Klewer Academic Pubilishers.

Cook, P. G. S., D.K.; Plummer, L.N.; Busenberg, E.; Schiff, S.L., 1995, Chlorofluorocarbons as tracers of groundwater transport processes in a shallow, silty sand aquifer: Water Resources Research, v. 31, no. 3, p. 425-434.

Friedman, I., Redfield, A. C., Schoen, B., Harris, J., 1964, The Variation of the Deuterium Content of Natural Waters in the Hydrologic Cycle: Reviews of Geophysics, v. 2, no. 1, p. 177-224.

GWMAP, G. W. M. a. A. P.-. 1999, Baseline Water Quality of Minnesota's Principal Aquifers: Twin Cities Metropolitan Region: Minnesota Pollution Control Agency.

MPCA, 1999a, Chloride and Flouride in Minnesota's Ground Water: Minnesota Pollution Control Agency.

MPCA, 1999b, Sulfate in Minnesota's Ground Water: Minnesota Pollution Control Agency.

MPCA, 1999c, Sodium and Potassium in Minnesota's Ground Water: Minnesota Pollution Control Agency.

MPCA, 1999d, Barium, Beryllium, Calcium, Magnesium and Strontium in Minnesota's Ground Water: Minnesota Pollution Control Agency.

MPCA, M. P. C. A., 1998, Baseline Water Quality of Minnesota's Principal Aquifers, Minnesota Pollution Control Agency.

Reston Chlorofluorocarbon Laboratory (R. C. L.), 2003, Collection and preservation of water samples for chlorofluorocarbon analysis in glass bottles with foil-lined caps: Reston, VA, p. 8.

Ruhl, J. F., Kanivetsky, R., Shmagin, B. A., Anoka County (MN), Carver County (MN), Dakota County (MN), Minnesota Board of Water & Soil Resources., and Geological Survey (U.S.), 2002, Estimates of recharge to unconfined aquifers and leakage to confined aquifers in the seven-county metropolitan area of Minneapolis-St. Paul, Minnesota, Water-resources investigations report ; 02-4092.: Mounds View, MN U.S. Dept. of the Interior U.S. Geological Survey ; Branch of Information Services [distributor], iv, 32 p.

Solomon, D. K., 2004, Error of CFC Dating, in Geochemistry Class, C. C., ed.: Northfield, MN.