Groundwater Geochemistry Above and Below the Decorah Aquitard

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Senior Integrative Exercise
May 16, 2005

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ABSTRACT

Winneshiek County in northeast Iowa contains unique topography and hydrogeology that makes it susceptible to the area’s agricultural contaminants. In 2005, water samples from wells drawing from the St. Peter Formation of the Cambrian-Ordovician Aquifer were collected from 13 locations throughout Decorah, Highlandville, Ridgeway, and Freeport townships in Winneshiek County. Wells sampled represented both new and older wells (built as early as 1963), as well as both cased and uncased wells. Additionally, samples were collected from 5 locations within the Galena Formation, a karst layer which overlies the Decorah Aquitard and the St. Peter. Samples were analyzed at Carleton College for anions (Fl\(^-\), Cl\(^-\), Br\(^-\), NO\(_3^-\), NO\(_2^-\), PO\(_4^{3-}\), and SO\(_4^{2-}\)) and cations (Na\(^+\), K\(^+\), Mg\(^+\), Ca\(^{2+}\), Li\(^+\), NH\(_4^+\)). Nitrate (NO\(_3^-\)), the major agricultural contaminant, was detected in 4 of the St. Peter wells (~3 mg/L to ~67 mg/L) and in all of the Galena wells (~24 mg/L to ~55 mg/L). Well casing appears to prevent nitrate contamination, as only one of the wells cased completely to the St. Peter contained nitrates. However, its concentrations were much lower than the uncased wells and much lower than the U.S. Environmental Protection Agency (USEPA) drinking water standard of 45 mg/L. One St. Peter sample from an area where the St. Peter is near the surface and is not overlain by the Decorah Aquitard, as well as one Galena sample, had nitrate levels which exceeded USEPA standards. Concentrations of Fl\(^-\), Cl\(^-\), SO\(_4^{2-}\), Na\(^+\), K\(^+\), Mg\(^+\), Ca\(^{2+}\) were also detected in some or all St. Peter wells. Overall, water from the Galena Formation displayed higher concentrations of nitrate, chloride, sodium, ammonium, potassium, magnesium, and calcium compared with the St. Peter Formation, but had lower concentrations of fluoride and sulfate. Discrepancies in the water quality between the Galena and the St. Peter samples shows the effectiveness of the Decorah Aquitard in keeping the newly-recharged Galena water from entering the St. Peter. Additionally, ion concentrations are related to whether or not the well is located in an area of direct recharge, and whether the ion in question came from anthropogenic or natural sources.

Keywords: Galena Formation, groundwater, nitrate, northeast Iowa, St. Peter Formation, Decorah Formation, Decorah Aquitard, Winneshiek County.
INTRODUCTION

Iowa, one of the nation’s leading agricultural states, dedicates nearly ninety percent of its area to farmland (Iowa Department of Agriculture and Land Stewardship, 2003) and annually applies 3 billion pounds of chemical fertilizers and 45 million pounds of pesticides to its land (Iowa Department of Natural Resources (DNR), 2000). Such chemicals run off into drainage tiles, lakes, and streams, and can make their way into the groundwater. Agricultural pollution is a special concern to the eighty percent of Iowans who obtain their drinking water from groundwater reserves (Prior et al., 2003). The groundwater of northeast Iowa, where the geology is conducive to deeper groundwater circulation, is particularly vulnerable to contamination (Libra et al., 1993). Additionally, the abundant cracks and sinkholes in the limestone and dolostone karst topography (Prior et al., 2003) and the local lack of Pleistocene glacial cover (Tjostem et al., 1977) provide locations for direct infiltration to the water table.

This study addresses the water geochemistry of the St. Peter Formation and Galena Formation within Winneshiek County, Iowa. It assesses the effectiveness of the Decorah Aquitard’s ability to keep the newly-recharged Galena water from entering the St. Peter, as well as the effectiveness of cased wells in keeping newly recharged water from entering private drinking wells within the St. Peter. It has already been shown that cased wells in Winneshiek County are more effective than uncased wells in keeping bacteria and nitrates from new water from entering the aquifer (Tjostem et al., 1977). This study provides a more current look at the discrepancies and examines other factors, such as well construction and hydrogeologic locations. A better understanding of water contamination patterns and well-casing effectiveness in Winneshiek County will allow
well owners and drillers to understand what type of well construction is most cost-effective and provides the most uncontaminated water. Groundwater contamination has already proven to be a pressing issue, as fifty-five percent of Iowa’s private wells contain coliform bacteria or excessive amounts of nitrates (Iowa DNR, 2000), which cause life-threatening conditions such as methemoglobinemia, or “blue baby syndrome” (Minnesota Pollution Control Agency (MPCA), 1998).

HYDROGEOLOGY

Stratigraphy
Northeastern Iowa consists of a sequence of Ordovician and Cambrian sedimentary rocks (Fig. 1) which contain aquifers and confining units (Fig. 3) which were deposited in what was the Hollandale Embayment, a shallow extension of the Paleozoic oceans (Ruhl et al., 1983). At one time, younger sediments were deposited on top of these units; however, later erosion removed the more recent deposition, leaving only the Ordovician and Cambrian layers intact (Tjostem et al., 1977). Consequently, while most of Iowa is covered with a thick layer of Pleistocene glacial clay that protects the bedrock, this layer is extremely thin in the “Driftless Area” of Alamakee County and eastern Winneshiek County (Tjostem et al., 1977). Because the bedrock is nearly uncovered, it is unprotected from contaminated surface water.

The uppermost bedrock unit consists of the Galena Formation (Fig. 3), a dolostone layer which contains many solution cavities which form along bedding planes and can serve as places to store water. Water can also be stored along vertical fractures which connect these cavities (Tjostem et al., 1977). The Galena is overlain by numerous sinkholes which allow a rapid flow of undiluted water containing silt, bacteria, and agricultural chemicals into the ground (Prior et al., 2003). In the general area of northeast
Figure 1. Iowa Bedrock formations, provided by Iowa DNR, 1998.

Figure 2. Location of the Driftless Area, which covers the eastern part of Winneshiek County.
<table>
<thead>
<tr>
<th>Era/System</th>
<th>Group/Formation</th>
<th>Typical Thickness (ft) in Winneshiek County</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cenozoic</td>
<td>Glacial drift and topsoil</td>
<td>thin to none</td>
</tr>
<tr>
<td>Quaternary</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ordovician</td>
<td>Galena dolostone</td>
<td>20-200 (most often &gt;120)</td>
</tr>
<tr>
<td></td>
<td>Decorah shale and limestone</td>
<td>0-53</td>
</tr>
<tr>
<td></td>
<td>Platteville limestone</td>
<td>25-40</td>
</tr>
<tr>
<td></td>
<td>Glenwood shale</td>
<td>0-12</td>
</tr>
<tr>
<td></td>
<td>St. Peter sandstone</td>
<td>60-70</td>
</tr>
<tr>
<td></td>
<td>Shakopee dolostone</td>
<td>~300</td>
</tr>
<tr>
<td>Paleozoic</td>
<td>Oneota dolostone</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cambrian</td>
<td>Jordan sandstone</td>
<td>~100</td>
</tr>
<tr>
<td></td>
<td>St. Lawrence dolostone</td>
<td>~75</td>
</tr>
<tr>
<td></td>
<td>Lone Rock</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wonewoc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Eau Claire</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mt. Simon sandstone</td>
<td>~200</td>
</tr>
<tr>
<td>Proterozoic</td>
<td>sandstone, igneous, metamorphic rocks</td>
<td>~1300</td>
</tr>
</tbody>
</table>

Figure 3. Stratigraphic section for Winneshiek County, Iowa.
Figure 4. Cross section from southeast to northeast Iowa. Modified from Prior et al., 2003.
Iowa, there are over 12,700 mapped sinkholes (Prior et al., 2003). Other possible sources of contamination include leakage through old wells which have not been properly sealed and agricultural drainage wells (Prior et al., 2003). Water that percolates down into the Galena Formation reaches the limestone and shale Decorah, Platteville, and Glenwood formations, referred to in this paper as the “Decorah Aquitard,” but also known as the Decorah-Platteville-Glenwood confining unit. Limestone is very soluble in water, offering no water filtration capabilities and allowing water to move through great distances relatively quickly (Tjostem et al., 1977). However, the downward movement is generally stopped when it comes into contact with the relatively impervious shale layers in the confining unit (Wheeler et al., 1988). At this contact point, water flows laterally and discharges as springs (Wheeler et al., 1988). Many of these springs are tributaries to the Upper Iowa River, which itself is a tributary that runs eastward into the Mississippi River.

Under the shale and limestone Decorah Aquitard is the Ordovician-Cambrian Aquifer, sometimes referred to as the Jordan Aquifer (Fig. 3). The aquifer contains the St. Peter Sandstone, Prairie du Chien Group (Shakopee and Oneota Formations), the Jordan Sandstone, and the St. Lawrence Dolostone (Prior, 2003). The St. Peter Sandstone, from where most private wells in northeast Iowa draw their water, consists of well-sorted, fine-to medium-grained sand (Lindgren, 1997) which is tightly packed, giving it natural filtering ability (Tjostem et al., 1977).

**Recharge and discharge**

Groundwater moves from areas of high hydraulic head to areas of lower head, and the direction it flows is dependent on locations of recharge and discharge (Lindgren,
1997). In addition, the rate at which groundwater flows is determined by the material which comprises the aquifer (Lindgren, 1997). Northeastern Iowa is unique from the rest of the state in that the Ordovician-Cambrian Aquifer recharges both directly and indirectly. Direct recharge occurs in places where upland areas are missing thick glacial drift (Burkart and Buchmiller, 1990), where the Decorah confining unit is missing, or where there is leakage from major streams (Lindgren, 1997). Regions of direct recharge and discharge create localized flow patterns throughout northeast Iowa (Burkart and Buchmiller, 1990). Indirect recharge occurs from overhead aquifers with a higher head when there is leakage within the adjacent confining unit (Burkart and Buckmiller, 1990). Hydrogeologists R.J. Mandle and A.L. Kontis (1992) simulate that water recharging from the glacial drift to the area’s aquifer is, on average, 0.45 inches per year, much higher than recharge to other aquifers in the Midwest. Most precipitation recharges to streams, so the recharge rate Mandle and Kontis determined is less than 1.5 percent of average annual precipitation (1992).

The aquifer discharges horizontally into the Mississippi River and its tributary streams and rivers (Ruhl et al., 1983) and wells within the aquifer, as well as vertically to underlying rock layers (Lindgren, 1997). In general, the eastern half of Winneshiek County is characterized as an area of direct recharge or discharge, and the western half is characterized as an area of recharge by vertical leakage from overlying aquifers through a confining unit (Burkart and Buchmiller, 1990).

**Formation thicknesses and slope**

After horizontal deposition, the sedimentary layers slowly tilted, creating a slant toward the southwest (Fig. 4), known as the “Iowa Sag” (Knudson, 1971). Today, there
<table>
<thead>
<tr>
<th>R10W</th>
<th>R09W</th>
<th>R08W</th>
<th>R07W</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>#57108, Sec. 22 1170'</td>
<td>#10555, Sec. 22 1230'</td>
<td>#55058, Sec. 22 1305'</td>
</tr>
<tr>
<td></td>
<td>clay: 1170-1150</td>
<td>topsoil: 1230-1228</td>
<td>soil: 1305-1290</td>
</tr>
<tr>
<td></td>
<td>shale/sand: 1150-1120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Galena: 1120-975</td>
<td>Galena: 1228-1050</td>
<td>Galena: 1290-1270</td>
</tr>
<tr>
<td>0</td>
<td>Decorah: 975-935</td>
<td>Decorah: 1050-1010</td>
<td>Decorah: 1270-1235</td>
</tr>
<tr>
<td></td>
<td>St. Peter: 883-810</td>
<td>St. Peter: 980-906</td>
<td>St. Peter: 1210-1195</td>
</tr>
<tr>
<td></td>
<td>(older strata at surface)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>#28173, Sec. 30 1270'</td>
<td>#54129, Sec 22 1140'</td>
<td>#57281, Sec. 22 980'</td>
</tr>
<tr>
<td></td>
<td>soil: 1270-1269</td>
<td>soil: 1140-1094</td>
<td>clay: 980-970</td>
</tr>
<tr>
<td></td>
<td>Wapsipinicon: -1050</td>
<td>Galena: 1094-924</td>
<td>clay: 1060-1055</td>
</tr>
<tr>
<td>9</td>
<td>Galena: 1050-850</td>
<td>Decorah: 924-850</td>
<td>loess (clay): 1080-1065</td>
</tr>
<tr>
<td>9</td>
<td>Decorah: 850-830</td>
<td>Platteville: -850</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Platteville: 850-844</td>
<td>Glenwood: 850-844</td>
<td></td>
</tr>
<tr>
<td></td>
<td>St. Peter: 844-781</td>
<td>St. Peter: 970-908</td>
<td>St. Peter: 1065-1050</td>
</tr>
<tr>
<td></td>
<td>(older strata at surface)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>#28202, Sec. 15 1210'</td>
<td>#31994, Sec. 21 1200'</td>
<td>#35463, Sec. 22 1030'</td>
</tr>
<tr>
<td></td>
<td>soil: 1210-1204</td>
<td>soil: 1200-1198</td>
<td>soil &amp; clay: 1030-1015</td>
</tr>
<tr>
<td>9</td>
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<td>Wapsipinicon: -1040</td>
<td>soil &amp; clay: 1125-1110</td>
</tr>
<tr>
<td>8</td>
<td>Decorah: 785-738</td>
<td>Decorah: 819-738</td>
<td>Decorah: 983-950</td>
</tr>
<tr>
<td>N</td>
<td>Platteville: 738-714</td>
<td>Platteville: 738-714</td>
<td>Platteville: 950-915</td>
</tr>
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<td>None: too deep</td>
<td>#56523, Sec. 16 1225'</td>
<td>#54104, Sec. 10 1100'</td>
<td>#35663, Sec. 22 1217'</td>
</tr>
<tr>
<td>T</td>
<td>clay: 1225-1215</td>
<td>clay: 1110-1078</td>
<td>soil &amp; clay: 1217-1208</td>
</tr>
<tr>
<td>9</td>
<td>Wapsipinicon: -925</td>
<td>Wapsipinicon: -925</td>
<td>Wapsipinicon: -1107</td>
</tr>
<tr>
<td>7</td>
<td>Galena: 925-705</td>
<td>Galena: 1078-820</td>
<td>Galena: 1107-887</td>
</tr>
<tr>
<td>7</td>
<td>Decorah: 705-669</td>
<td>Decorah: 820-673</td>
<td>Decorah: 887-738</td>
</tr>
<tr>
<td>N</td>
<td>Platteville: 669-631</td>
<td>Platteville: -738</td>
<td>Platteville: -807</td>
</tr>
<tr>
<td>7</td>
<td>Glenwood: 631-610</td>
<td>Glenwood: 738-731</td>
<td>Glenwood: -807</td>
</tr>
<tr>
<td>7</td>
<td>St. Peter: 610-563</td>
<td>St. Peter: 731-675</td>
<td>St. Peter: 807-752</td>
</tr>
<tr>
<td>None: too deep</td>
<td>None: too deep</td>
<td>None: too deep</td>
<td>None: too deep</td>
</tr>
<tr>
<td>T</td>
<td>#54112, Sec. 21 1204'</td>
<td>#20274, Sec. 21 1245'</td>
<td>#20274, Sec. 21 1245'</td>
</tr>
<tr>
<td>9</td>
<td>None: too deep</td>
<td>None: too deep</td>
<td>None: too deep</td>
</tr>
<tr>
<td>6</td>
<td>soil &amp; clay: 1204-1184</td>
<td>soil &amp; clay: 1204-1184</td>
<td>soil &amp; clay: 1245-1225</td>
</tr>
<tr>
<td>6</td>
<td>Decorah: 796-720</td>
<td>Decorah: 796-720</td>
<td>Galena: 1040-818</td>
</tr>
<tr>
<td>6</td>
<td>Platteville: -706</td>
<td>Platteville: -706</td>
<td>Decorah: 818-765</td>
</tr>
</tbody>
</table>

Figure 5. Stratigraphic location of Decorah and St. Peter formations in Winneshiek County, Iowa, by township, using data from Iowa Geological Survey (2005).
is a difference of over 400 feet in elevation in the depth of the St. Peter in only about 16
miles, or about 25 feet per mile from southwest to northeast (Fig. 4). The slope has
considerable impact on which formations are present in a given area. For example, in the
southwestern part of the county, St. Peter is overlain by Galena and Maquoketa.
However, in the northwest, central, and southeastern part of the county, St. Peter is
overlain by Galena only, and in the northeastern part of the county the Galena and St.
Peter are absent.

**WELL SELECTION AND METHODS**

I collected water samples from both the St. Peter Formation and the Galena
Formation of Winneshiek County, Iowa. In January 2005, I collected groundwater
samples from 13 locations within Winneshiek County, Iowa within the quadrangles
Decorah, Highlandville, Ridgeway, and Freeport (Fig. 6). Selection of the St. Peter wells
was based on the following criteria: wells ended in the St. Peter formation or within a few
feet below, wells provided access to unfiltered water, well logs or driller’s logs were
available and complete—showing records of depth, stratigraphy, and (if applicable)
casing. Well selection was further categorized as “cased” and “uncased” wells. I
qualified a “cased” well as one that is cased through the Decorah Aquitard into the St.
Peter, and an “uncased” well as one with casing which ends before the Decorah Aquitard.
I selected wells in order to represent both new and old wells, with construction dates
ranging from the 1960’s until present. Background information for the wells that were
analyzed is listed in Table 1. While I tried to test only unsoftened water, I later realized
that three faucets were unknowingly softened. All wells tested are currently private wells
not used for agricultural or manufacturing purposes. I obtained information on the wells online through the Iowa Geological Survey (2005) and by talking with individual well owners.

Additionally, water samples were collected from five locations within the Galena Formation of Winneshiek County during February, 2005. Because there are very few private wells that end in this formation, these samples were collected from natural springs. Sampling locations included: Upper Iowa River, as well as where Sand Canyon Creek, Malanaphy Springs, Dunning Springs, and Twin Springs first outcrop from the bedrock (Fig. 6).

Although CFC-analysis was ultimately not performed, all samples were collected in 4 oz. SKS glass bottles with foil-lined caps and sealed with electrical tape according to the methods of the Reston Chlorofluorocarbon Laboratory (Reston, 2003). At Carleton College, samples were analyzed using a Dionex Ion 600 Chromatograph (IC) to test for cations: Na\(^+\), K\(^+\), Mg\(^+\), Ca\(^{2+}\), Li\(^+\), NH\(_4\)^+\, and anions: F\(^-\), Cl\(^-\), Br\(^-\), NO\(_2\)^-, NO\(_3\)^-, PO\(_4\)^{3-}\, and SO\(_4\)^{2-}\,. 
<table>
<thead>
<tr>
<th>Well owner</th>
<th>Well number</th>
<th>Location</th>
<th>Quad map</th>
<th>Elevation (ft)</th>
<th>Total depth (ft)</th>
<th>Casing depth (ft)</th>
<th>Depth to bedrock (ft)</th>
<th>Year drilled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friest</td>
<td>56552</td>
<td>T99N R8W Sec. 24 SW NE</td>
<td>Highlandville</td>
<td>980</td>
<td>103</td>
<td>Partially cased (unknown depth)</td>
<td>39</td>
<td>1972</td>
</tr>
<tr>
<td>Kittleson</td>
<td>56548</td>
<td>T99N R9W Sec. 26 NE SE</td>
<td>Decorah</td>
<td>955</td>
<td>197</td>
<td>no casing</td>
<td>unknown</td>
<td>1968</td>
</tr>
<tr>
<td>Henning</td>
<td>56532</td>
<td>T98N R8W Sec. 14 NE SE</td>
<td>Decorah</td>
<td>977</td>
<td>175</td>
<td>no casing</td>
<td>unknown</td>
<td>13</td>
</tr>
<tr>
<td>Meade</td>
<td>59087</td>
<td>T99N R8W Sec. 24</td>
<td>Highlandville</td>
<td>983</td>
<td>120</td>
<td>79</td>
<td>15</td>
<td>2004</td>
</tr>
<tr>
<td>Nesset</td>
<td>16068</td>
<td>T98N R8W Sec. 19 NE SE SW</td>
<td>Decorah</td>
<td>1020</td>
<td>230</td>
<td>unknown</td>
<td>2</td>
<td>1963</td>
</tr>
<tr>
<td>Sullivan</td>
<td>51110</td>
<td>T98 R9W Sec. 2 NE NW</td>
<td>Decorah</td>
<td>1132</td>
<td>360</td>
<td>306</td>
<td>19</td>
<td>1999</td>
</tr>
<tr>
<td>Smith</td>
<td>54307</td>
<td>T99N R9W Sec. 24 SE SE</td>
<td>Decorah</td>
<td>952</td>
<td>140</td>
<td>+100</td>
<td>20</td>
<td>1988</td>
</tr>
<tr>
<td>Linnane</td>
<td>56556</td>
<td>T99N R9W Sec. 26</td>
<td>Ridgeway</td>
<td>983</td>
<td>163</td>
<td>unknown</td>
<td>13</td>
<td>1970</td>
</tr>
<tr>
<td>Kratz</td>
<td>58583</td>
<td>T98N R9W Sec. 24 SW SE</td>
<td>Decorah</td>
<td>1142</td>
<td>456</td>
<td>396</td>
<td>35</td>
<td>2004</td>
</tr>
<tr>
<td>Bishop</td>
<td>46328</td>
<td>T98N R9W Sec. 26 NE SW</td>
<td>Decorah</td>
<td>1205</td>
<td>550</td>
<td>500</td>
<td>30</td>
<td>1998</td>
</tr>
<tr>
<td>McCaffrey</td>
<td>35672</td>
<td>T98 N R8W Sec. 19 NE SW</td>
<td>Decorah</td>
<td>995</td>
<td>240</td>
<td>185</td>
<td>18</td>
<td>1995</td>
</tr>
<tr>
<td>Wieseler</td>
<td>59370</td>
<td>T99N R8W Sec. 34 NW NE NW</td>
<td>Decorah</td>
<td>unknown</td>
<td>380</td>
<td>335</td>
<td>30</td>
<td>2004</td>
</tr>
<tr>
<td>Lecander</td>
<td>57897</td>
<td>T99N R8W Sec. 19 SW SW NE</td>
<td>Decorah</td>
<td>unknown</td>
<td>261</td>
<td>159.75</td>
<td>20</td>
<td>2003</td>
</tr>
</tbody>
</table>
Figure 6. Township map for Winneshiek County, Iowa, showing sampling locations for Galena and St. Peter Formations and where nitrate was present. Each township is generally 6x6 miles, except in the northwest.
RESULTS

St. Peter Formation

Nitrates

The IC results showed that four of the thirteen St. Peter groundwater samples contained nitrates (Table 2), which were found in concentrations of 2.99 mg/L to 67.11 mg/L, expressed as NO$_3^-$ (0.68 mg/L to 15.15 as NO$_3$-N). Nitrates were detected in wells from both Highlandville and Decorah. Wells with nitrates had construction dates ranging from 1968 to 2004 (Table 1). Only one of the wells cased completely to the St. Peter contained nitrates; however, its concentrations (2.99 mg/L) were much lower than the uncased or partially uncased wells, and much lower than the USEPA drinking water standard of 45 mg/L (Prior et al., 2003).

Other Anions: sulfate, chloride, and fluoride

Nitrate, chloride, fluoride, and sulfate were detected out of the six types of anions for which the samples were tested (Table 2). There was no presence of bromide, phosphate, or nitrite in any of the samples. Very small concentrations of fluoride were found in six samples, with the highest concentration being 0.13 mg/L. Chloride was detected in all samples, displaying the large range of 0.63 mg/L to 44.18 mg/L. High concentrations of sulfate were found in all samples, ranging from 9.08 mg/L to 39.36 mg/L. In general, wells with high nitrates tended to also have high concentrations of chloride. A similar but weaker correlation was found linking these anions to fluoride. However, wells with high nitrates and chloride did not have overall higher amounts of sulfate; sulfate could be found in high amounts even in wells with no nitrate.
Cations: sodium, potassium, magnesium, calcium, and ammonium

Sodium, potassium, magnesium, and calcium were detected in all samples (Table 2). Discounting samples with softened water, the Friest sample had the highest concentration of sodium, containing 7.67 mg/L. This well also had the highest amount of calcium (129.54 mg/L). Potassium concentrations were consistently low, ranging from 0.40 mg/L to 3.75 mg/L, and were found in all tested samples. Magnesium was also found in all samples, ranging from 0.12 mg/L to 34.47 mg/L. All samples lacked detectable amounts of lithium and ammonium.

Galena Formation

Overall, water from the Galena Formation displayed higher concentrations of nitrate, chloride, sodium, and potassium, magnesium, and calcium compared with water from the cased St. Peter wells (Table 3). The Galena had no fluoride and lower concentrations of sulfate. Nitrates were consistently high (Table 4), with concentrations over the potability standards (45 mg/L) in the Upper Iowa River (54.76 mg/L). While nitrate concentrations in the other Galena sources were also substantial, one St. Peter well had higher concentrations. Sulfate was found in all samples, ranging from 3.13 mg/L to 20.88 mg/L. Chloride concentrations were also consistently high, but did not surpass concentrations of the two most contaminated St. Peter wells. Sodium concentrations were as high as 12.97 mg/L (Table 5), much higher than any St. Peter well which was unsoftened. Potassium was also higher in the Galena water, up to 5.87 mg/L. Magnesium and calcium concentrations, while also high in all Galena wells, were sometimes lower than what was found in the St. Peter wells.
Table 2. Anion and cation concentrations (mg/L) of St. Peter wells

<table>
<thead>
<tr>
<th>Well owner</th>
<th>Nitrate</th>
<th>Nitrate- N</th>
<th>Fluoride</th>
<th>Chloride</th>
<th>Sulfate</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Magnesium</th>
<th>Calcium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friest</td>
<td>67.11</td>
<td>15.15</td>
<td>0.13</td>
<td>44.18</td>
<td>39.36</td>
<td>7.67</td>
<td>1.30</td>
<td>24.74</td>
<td>129.54</td>
</tr>
<tr>
<td>Kittleson</td>
<td>16.87</td>
<td>3.81</td>
<td>0.10</td>
<td>38.76</td>
<td>18.48</td>
<td>3.89</td>
<td>1.57</td>
<td>32.06</td>
<td>94.71</td>
</tr>
<tr>
<td>Henning</td>
<td>15.30</td>
<td>3.45</td>
<td>0.12</td>
<td>10.31</td>
<td>20.60</td>
<td>7.20</td>
<td>3.75</td>
<td>31.88</td>
<td>127.03</td>
</tr>
<tr>
<td>Meade</td>
<td>2.99</td>
<td>0.68</td>
<td>0</td>
<td>3.92</td>
<td>20.17</td>
<td>3.82</td>
<td>0.82</td>
<td>14.26</td>
<td>25.47</td>
</tr>
<tr>
<td>Nesset</td>
<td>0</td>
<td>0</td>
<td>0.09</td>
<td>1.40</td>
<td>21.01</td>
<td>4.13</td>
<td>2.09</td>
<td>34.47</td>
<td>94.15</td>
</tr>
<tr>
<td>Sullivan*</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.95</td>
<td>9.08</td>
<td>185.70</td>
<td>0.40</td>
<td>0.12</td>
<td>0.58</td>
</tr>
<tr>
<td>Smith</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.63</td>
<td>18.05</td>
<td>4.26</td>
<td>1.61</td>
<td>33.40</td>
<td>100.36</td>
</tr>
<tr>
<td>Linnane</td>
<td>0</td>
<td>0</td>
<td>0.07</td>
<td>0.77</td>
<td>17.50</td>
<td>6.60</td>
<td>1.42</td>
<td>24.37</td>
<td>43.74</td>
</tr>
<tr>
<td>Kratz</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.73</td>
<td>23.08</td>
<td>4.16</td>
<td>1.55</td>
<td>31.90</td>
<td>56.42</td>
</tr>
<tr>
<td>Bishop</td>
<td>0</td>
<td>0</td>
<td>0.08</td>
<td>1.35</td>
<td>20.90</td>
<td>4.95</td>
<td>2.22</td>
<td>34.33</td>
<td>91.75</td>
</tr>
<tr>
<td>McCaffrey*</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.52</td>
<td>19.93</td>
<td>186.88</td>
<td>0.87</td>
<td>0.22</td>
<td>0.67</td>
</tr>
<tr>
<td>Wieseler*</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.41</td>
<td>20.22</td>
<td>194.77</td>
<td>0.37</td>
<td>0.14</td>
<td>0.72</td>
</tr>
<tr>
<td>Lecander</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.56</td>
<td>22.25</td>
<td>3.90</td>
<td>1.64</td>
<td>32.28</td>
<td>91.91</td>
</tr>
</tbody>
</table>

*Note: The Sullivan, McCaffrey, and Wieseler taps unknowingly provided softened water, artificially increasing the sodium content and reducing the magnesium and calcium content.

Table 3. Average anion and cation concentrations (mg/L) of St. Peter and Galena Formations

<table>
<thead>
<tr>
<th>Sample set</th>
<th>Nitrate</th>
<th>Chloride</th>
<th>Sulfate</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Magnesium</th>
<th>Calcium</th>
<th>Ammonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncased St. Peter</td>
<td>33.09</td>
<td>31.08</td>
<td>26.14</td>
<td>6.25</td>
<td>2.21</td>
<td>29.54</td>
<td>117.10</td>
<td>0</td>
</tr>
<tr>
<td>Cased St. Peter</td>
<td>0.299</td>
<td>1.58</td>
<td>17.31</td>
<td>4.55</td>
<td>1.62</td>
<td>29.29</td>
<td>71.97</td>
<td>0</td>
</tr>
<tr>
<td>St. Peter overall</td>
<td>7.87</td>
<td>8.39</td>
<td>19.35</td>
<td>5.06</td>
<td>1.80</td>
<td>29.36</td>
<td>85.51</td>
<td>0</td>
</tr>
<tr>
<td>(both cased and uncased)</td>
<td>7.87</td>
<td>8.39</td>
<td>19.35</td>
<td>5.06</td>
<td>1.80</td>
<td>29.36</td>
<td>85.51</td>
<td>0</td>
</tr>
<tr>
<td>Galena</td>
<td>32.77</td>
<td>16.68</td>
<td>15.00</td>
<td>9.66</td>
<td>3.57</td>
<td>42.47</td>
<td>128.75</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Table 4. Anion concentrations (mg/L) of Galena water

<table>
<thead>
<tr>
<th>Water source</th>
<th>Nitrate</th>
<th>NO₃-N</th>
<th>Chloride</th>
<th>Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper IA River</td>
<td>54.77</td>
<td>12.36</td>
<td>16.08</td>
<td>13.44</td>
</tr>
<tr>
<td>Sand Canyon Creek</td>
<td>23.38</td>
<td>5.28</td>
<td>21.63</td>
<td>20.88</td>
</tr>
<tr>
<td>Twin Springs</td>
<td>37.75</td>
<td>8.52</td>
<td>16.58</td>
<td>13.13</td>
</tr>
<tr>
<td>Dunning Springs</td>
<td>24.28</td>
<td>5.48</td>
<td>14.71</td>
<td>13.87</td>
</tr>
<tr>
<td>Malanaphy Springs</td>
<td>23.70</td>
<td>5.35</td>
<td>14.41</td>
<td>13.68</td>
</tr>
</tbody>
</table>

Table 5. Cation concentrations (mg/L) of Galena water

<table>
<thead>
<tr>
<th>Water source</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Magnesium</th>
<th>Calcium</th>
<th>Ammonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Iowa River</td>
<td>12.97</td>
<td>5.87</td>
<td>30.75</td>
<td>103.12</td>
<td>0.92</td>
</tr>
<tr>
<td>Sand Canyon Creek</td>
<td>8.75</td>
<td>3.32</td>
<td>46.49</td>
<td>146.80</td>
<td>0</td>
</tr>
<tr>
<td>Twin Springs</td>
<td>12.03</td>
<td>3.99</td>
<td>45.35</td>
<td>117.77</td>
<td>0</td>
</tr>
<tr>
<td>Dunning Springs</td>
<td>11.14</td>
<td>2.09</td>
<td>47.43</td>
<td>142.64</td>
<td>0</td>
</tr>
<tr>
<td>Malanaphy Springs</td>
<td>9.69</td>
<td>2.57</td>
<td>42.31</td>
<td>133.40</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 7. Ion concentrations for a) the St. Peter well samples and b) the Galena sources. St. Peter well owners with asterisks had softened water, and sodium, calcium, and magnesium for these wells are not displayed here.
Figure 8: Average concentrations of major ions found in the St. Peter and Galena Formations.

*Note: Nitrate, chloride, sodium, and potassium are of anthropogenic sources.
DISCUSSION

Overall, the data displayed several trends. There were discrepancies between Galena and St. Peter formations, as well as within formations themselves. Differences within the St. Peter Formation can generally be attributed to three main factors: well casing depth, whether or not the well is located in an area of direct recharge, and whether the ion in question came from anthropogenic or natural sources. These trends will now be discussed in more detail, with an emphasis on the contamination patterns of nitrate, the ion which poses the most serious concern to ground water consumers.

**Nitrate (NO$_3^-$) Contamination Patterns**

Nitrate is a major agricultural chemical which comes from fertilizer and can contaminate a water supply when it leaks into the ground or runs off into streams and rivers. Since it does not occur naturally in groundwater, one can expect that any amount of nitrate present in a water sample has come from the surface. In Winneshiek County, water that exists in the Galena Formation, which is near the surface and is recharged quickly through sinkholes and limestone cracks, has been more recently recharged than St. Peter water, which exists at a deeper depth and is substantially protected from new, high nitrate water by the overlying Decorah confining unit. It then is no surprise that in comparing the Galena and St. Peter water, nitrate levels were generally lower in the St. Peter, especially in the cased wells (Fig. 7 and 8). This assertion is also supported by a previous (unpublished) study which age-dated the water from the Cambrian-Ordovician Aquifer in southeastern Minnesota and found a correlation between higher nitrate concentrations and more recent recharge dates (James et al., 2004). Additionally, the discrepancy between the shallower and deeper sources fits generally into the State-Wide
Rural Well-Water Survey’s (SWRL) previous findings. (In 1990, the SWRL found that wells less than 100 feet deep represented 89% of the total Iowa wells tested that had nitrate concentrations greater than the USEPA’s standards for drinking water (Sadorf and Linhart, 2000). However, the SWRL only tested alluvial aquifers, so there is no way to directly compare the results of these two studies; only the general trend of higher contaminants in the shallower aquifers is relevant.)

Within the St. Peter Formation samples, it is evident that nitrate content is primarily dependent on well casement depth and whether areas directly above and near the well are overlain by the Decorah Aquitard. All of the uncased or partially uncased wells contained nitrates (as much as \(~67\) mg/L), whereas only one of the ten fully cased wells contained nitrates—but in much lower concentrations (less than 3 mg/L) (Table 1, Fig. 7). The deeper casing of the less contaminated wells assures that the water which is being drawn into wells was recharged less recently than high-nitrate water which could leak in from the surface. These data coincide with the results of Tjostem’s study of Winneshiek County wells (1977). Tjostem’s study found 1.7 mg/L to be the average nitrate concentration of cased wells terminating in the St. Peter, while the average nitrate concentration of uncased wells terminating in the St. Peter was 28.9 mg/L (Tjostem et al., 1977). However, Tjostem’s study did not describe where the high-nitrate St. Peter wells were located within Winneshiek County.

The Friest well had particularly high nitrates even for an uncased well, and the cased Meade well had some nitrates, while none of the other cased wells did, suggesting that well casing is not the only important determinant of nitrate concentration. These higher nitrate instances can be explained by the stratigraphy at the wells’ locations. Both
of these wells are located in the eastern half of the county (Fig. 6), an area characterized by direct recharge and less glacial cover (Burkart and Buchmiller, 1990). Additionally, the Decorah Aquitard is missing in areas one mile or less distant from the cased Meade well, and the Aquitard is entirely missing around the uncased Friest well (Fig. 4). Looking at this, it is clear that new surface recharge has entered into the St. Peter at these locations, bringing with it a recent influx of nitrates, raising concentrations in these two wells.

Additionally, it is important to note the factors which did not seem to influence the nitrate levels in St. Peter wells. For instance, the construction date of the wells differ significantly, ranging from 1963 to 2004 (Table 1). However, the oldest of these wells—the Nesset well (1963)—had no nitrates, while one of the youngest wells—the Meade well (2004)—did have nitrates. (Three wells built before 1974 had nitrates; however, these wells were also uncased; therefore, contamination can be attributed mostly to that.) This evidence shows that even fairly old wells can still be very effective in keeping out leakage, as long as they are cased, but that even brand new cased wells may become slightly contaminated if they are in a location of direct recharge.

The Galena also offers some important insights into nitrate contamination patterns. The Upper Iowa River had more than twice the nitrates (54.76 mg/L) compared to all other Galena sources (23.3-24.28 mg/L), except for Twin Springs (37.75 mg/L). Since the Upper Iowa is fed by the watershed’s springs and creeks, it accumulates the sum of all of the nitrates which are flowing into it, and it therefore makes sense that the river would display especially high concentrations.
One important influence on nitrate levels that was not examined in this study was the effect of precipitation. Studies have concluded that rainfall temporarily increases Iowa nitrate concentrations (Wheeler et al., 1989) and that nitrates are highest during the spring and summer (Libra et al., 1993). Average nitrates for Iowa wells are generally found in mid-fall, around October (Libra et al., 1993). Since this study was performed during the winter, at a time of low recharge, the nitrate values that were found in these studies may be much lower than what they could be under more wet circumstances. However, the cased wells showing no nitrate contamination are probably protected by the Decorah Aquitard from such seasonal fluctuations.

High nitrates are associated with health problems, making them a special concern to well owners. Two samples—the Upper Iowa River and the Friest well—had nitrate ($\text{NO}_3^-$) above the USEPA maximum contaminant level (MCL) of 45 mg/L (Prior et al., 2003). In high amounts, nitrates can cause “blue baby syndrome” or methemoglobinemia, a dangerous disease which occurs when the oxygen and bacteria in the stomach oxidize nitrates into nitrites, severely limiting the blood’s capacity to carry oxygen (MCPA, 1998).

Once nitrates get into the groundwater system, they are very hard to remove. In order for nitrate concentrations to be reduced, nitrate must either be diluted or undergo biological transformation by microbes (MPCA, 1998b). However, both of these processes are difficult. Dilution can only work as long as additional nitrate is not added, and biological transformations can only occur once oxygen has been depleted by microbes, then forcing microbes to use nitrate as they would use oxygen (MPCA, 1998b). With these difficulties in mind, it seems like the best way to manage nitrate
concentrations is to limit the application of fertilizer throughout the watershed to recommended amounts to prevent excess nitrates from entering the water supply.

**Other anions: sulfate, chloride, and fluoride**

Examining other ions is also important in helping us to better understand groundwater flow and contamination patterns. Sulfate was the most prevalent anion, found in high concentrations in all samples, ranging from 9.08 mg/L to 39.36 mg/L in the St. Peter samples and 3.17 mg/L to 20.88 mg/L in the Galena samples (Fig. 7). Unlike nitrate, sulfate can come from natural sources, such as gypsum and pyrite contained in the aquifers (James et al., 2004), so the presence of sulfate does not necessarily indicate contamination. The non-anthropogenic source of sulfate possibly explains why cased St. Peter wells with no nitrates still exhibit high sulfate concentrations and why sulfate was found in higher concentrations in the St. Peter than in the Galena samples. However, there are also anthropogenic sources of sulfate, such as fertilizers and animal waste, and it can be deposited in the ground by precipitation of oxidized sulfur from fossil fuel combustion (James et al., 2004). There is no maximum contaminant level for sulfate. However, since high amounts of sulfate cause an unpleasant taste in drinking water and sometimes induce laxative effects, there is a maximum recommended level of 250 mg/L—a level much higher than contained in any of the samples tested in this study.

Chloride was also detected in all samples from both the Galena and the St. Peter (Fig. 7). Concentrations were consistently high in the Galena sources (14.41 mg/L to 21.63 mg/L), but displayed a great range in the St. Peter wells (0.11 mg/L to 44.18 mg/L). It is interesting to note that some of the St. Peter concentrations surpassed the Galena concentrations. The four highest concentrations of nitrates in the St. Peter wells
corresponded, in order, with the four highest chloride concentrations, indicating that the two chemicals came from a similar water source. Chloride can occur naturally in the mineral halite (MPCA, 1999a), but it can also come from road salt—which is distributed heavily on the Winneshiek County rural and city roads during the winter seasons—as well as from fertilizers and human and animal waste (MPCA, 1999a). Like sulfate, there is no health-based standard for chloride. However, chloride can corrode pipes and combine with sodium to create salty tasting drinking water; thus, it is recommended that chloride concentrations not exceed 250 mg/L (Prior et al., 2003).

Fluoride was found only in some of the St. Peter wells, in small amounts which never exceeded 0.13 mg/L (Table 2). Here, fluoride was found in all of the wells which were not fully cased, as well as in three wells which were fully cased. The amounts of fluoride were well under the recommended maximum level (2.0 mg/L) and the MCL (4.0 mg/L), which were set to protect drinking water consumers’ dental health (Prior et al., 2003). Fluoride is found in phosphorous fertilizers (MCPA, 1999a) as well as in limestone and dolostone in the form of fluorite (James et al., 2004). Because fluorite was only found in the deeper, St. Peter wells and not the Galena sources, the source of the fluoride was probably from within the bedrock. Generally, fluoride can also come from igneous rocks and industrial sites (MPCA, 1999a), neither of which exist in the study area.

Cations: Sodium, Potassium, Magnesium, Calcium, Ammonium

Discounting softened water samples from the St. Peter, Galena water showed higher amounts of sodium (Fig.6), indicating a surficial source, such as road salt or animal waste (MPCA, 1999b). While sodium can make water taste salty and lead to hypertension (MPCA, 1999b), there is no standard contaminant level for it (Prior et al.,
Galena samples also had higher potassium concentrations than St. Peter samples, again indicating surficial contamination, such as fertilizer (MPCA, 1999b). Potassium is less mobile in soil than sodium, which offers an explanation as to why it is found in lower concentrations (MPCA, 1999b). The highest potassium concentration, 5.87 mg/L, which was found in the Upper Iowa River sample, is essentially harmless; there are no great health threats associated with potassium. Sodium and potassium concentrations in groundwater increase with residence time, which may lead to higher concentrations in deeper aquifers over time (MCPA, 1999b). Because concentrations can be elevated from the fertilizer on the surface and also in deeper aquifers over time, high potassium and sodium concentrations are not well correlated with recharge age. It is not surprising, then, that the various St. Peter wells show no correlation between casing and potassium and sodium. However, the respectively higher levels found in the Galena sources indicate that surficial contamination has more of an effect on concentrations than residence time does.

Calcium and magnesium are fairly soluble ions which are ubiquitous in limestone and dolostone (MPCA, 1999c), explaining why there was a higher overall concentration of these ions in the Galena Formation than in the St. Peter. There are no major anthropogenic sources of these ions in the study area. Additionally, there are no known health problems associated with calcium or magnesium, and there is no recommended maximum level (MPCA, 1999c). However, when calcium plus magnesium concentrations exceed 100 mg/L, water is generally classified as “hard” water (MPCA, 1999c). Concentrations this high may cause scaling of pipes (MPCA, 1999c) and may limit the lathering ability of soap (Prior et al., 2003). All unsoftened private wells...
displayed calcium plus magnesium concentrations higher than 100 mg/L (~124 to ~159 mg/L). It is evident softening well water drastically reduces magnesium and calcium concentrations, since these provided concentrations of less than 1 mg/L.

Ammonium was detected in small amounts in the Upper Iowa River in the Galena Formation, but in no other samples from either formation (Fig. 7). Ammonium (NH$_4^+$) is derived from ammonia (NH$_3$), which is found in fertilizers (MPCA, 1998a). It is probable that the reason it is not found in the other samples is because it has been oxidized into nitrate (NO$_3^-$). However, a local source of nitrogen (usually in ammonia), such as fertilizer, waste from a feedlot, or a leaking septic system, can allow nitrate and ammonia to exist together (MPCA, 1998a), as in the Upper Iowa River sample.

**Implications**

Water in Iowa’s deepest aquifers has been age-dated by radiocarbon isotopes to be over 10,000 years old (Prior et al., 2003), suggesting that man-made pollutants could have a very long residency in one of our most valuable resources. Age-dating would allow us to quantify the groundwater susceptibility by determining how long it takes for contaminants to reach the St. Peter Formation of the Ordovician-Cambrian Aquifer and how long it takes for the groundwater to purge itself of contaminants. Tritium age-dating of alluvial aquifers was assessed during the State-Wide Rural Well-Water Survey (SWRL) by the Iowa Department of Natural Resources (DNR) in conjunction with the University of Iowa (Libra et al., 1994; Libra, et al., 1993; Rex et al., 1993; Thompson, 1986), but as of yet, the SWRL has not age-dated the Ordovician-Cambrian Aquifer.

While it is important to acknowledge that many pollutants are a threat to the environment and the health of the local people and animals that rely on the aquifer as a
source of drinking water, we must remember that our pollution does not just have local effects. Many of the locally-produced contaminants are very mobile in water and can spread throughout the water systems. For instance, it is estimated that 25% of the nitrates which flow into the Gulf of Mexico from the Mississippi River originate from Iowa (Iowa DNR, 2000). We must think and act responsibly to protect not only our own water supply, but also the water of others.

CONCLUSIONS

Overall, concentrations of anthropogenic ions (nitrate, sodium, chloride, and potassium) were higher in the Galena Formation than in the underlying St. Peter Formation, which is protected from recharge by the nearly impermeable Decorah Aquitard. The sharp discrepancy between the Galena and St. Peter pollution levels is of particular importance, since it shows how effectively the Decorah Aquitard prevents contaminants from leaking from the Galena into the St. Peter drinking water. However, even some of the St. Peter wells were contaminated with large amounts of nitrates and other ions, illustrating that the presence of the Decorah Aquitard itself is not enough to assure good water quality; well casing and is also essential. Additionally, hydrogeologic location was an important factor in water quality. Wells in the eastern part of Winneshiek County, which were located in an area of direct recharge, contained higher nitrates than other wells of their type (both cased and uncased).
ACKNOWLEDGEMENTS

I would like to thank my dad, Karl Knudson, for the tremendous energy, knowledge, and curiosity he shared with me about this project—at one point even wading through an icy, water-filled cave to collect a sample for me. Also, I would like to thank Aistis Tumas for reading my drafts, giving me endless support, and driving me to Decorah multiple times to collect samples. Of course, I could not have done my project without the help of my advisor, Professor Bereket Haileab, who encouraged me, read and commented on my paper, and spent several hours helping me run my samples through the IC. Additionally, I am so grateful towards Professor John Tjostem and Professor Jean Young of Luther College, for starting me off in the right direction with their valuable insight into the local geology. I would also like to give my appreciation to all of the well owners who allowed me to take samples from their wells. Thanks also to Professor Clint Cowan for reading and commenting on my paper, and Professor Deborah Gross of Carleton College, for explaining some of the details of groundwater chemistry.
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