Groundwater flow and geochemistry at Greenwoods Conservancy

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INTRODUCTION

Greenwoods Conservancy is located on the northern edge of the Appalachian plateau in central New York (latitude 42.719, longitude -75.098). Well-developed stream networks etch the region, which is underlain by gently southwest dipping sedimentary Devonian age rocks. Glaciers repeatedly advanced over this region during the Pleistocene epoch, and they scoured rock basins into the uplands, draped till sheets over the landscape, and mound moraines in trunk valleys. Cranberry Bog rests in one of these rock basins. Fractures in bedrock are visible in a few places in and around Greenwoods, and linear topographic features appear to follow the trend of these fractures. One such fracture runs right through the east side of Cranberry Bog. This project reports on the orientation of fractures exposed in bedrock around Greenwoods, and whether groundwater geochemistry is distinctive around fractures. One might hypothesize that deeper water is rising toward the surface along vertical fractures, and thus would have a measurably different chemistry from near surface waters. Several shallow dug wells (1-10 m depth) and 3 drilled deep wells (>40 m deep) were sampled extensively as a means of testing the hypothesis (Figure 1).

The main geologic layers in this region are, from youngest to oldest: stream and lake deposits; glacial drift; the Moscow formation (mostly shale and siltstone); the Panther Mountain formation (mostly shale and siltstone); the Marcellus formation (black shale, shale and limestone); and the Onondaga formation (mostly limestone). See Figure 2 below for a geologic cross section under Greenwoods. The Greenwoods Conservancy study deals mainly with the Moscow formation and the glacial till that lies above it, and water draining from those units.

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Figure 1. Topographic map displaying sampling locations, the regional fracture, and the locations where strike and dips were taken. The cluster of dots at the top of the map and just south of Cranberry Bog represent where the strike and dips were taken.

Figure 2. Geologic formations below Greenwoods Conservancy. (NYS Museum, 1999)
The Moscow formation represents a marine environment, ranging from deeper water where black shale accumulated, to shallower depths where thin ripple-marked sandstone beds and occasional marine fossils were deposited. The upper portion of the Moscow formation grades into terrestrial deposits. It underlies the Unadilla formation. The Panther Mountain formation consists mostly of shale layers, with lesser amounts of siltstone and sandstone beds. It underlies the Moscow formation (NYS Museum, 1999).

The Marcellus formation covers a wide region, from New York to Ohio, West Virginia, Pennsylvania and Maryland. It consists of black shale and occasional beds of medium-gray shale and limestone nodules or beds of dark gray to black limestone. The Onondaga formation consists of limestone, dolostone, and shale beds. The Onondaga was deposited in a shallow warm tropical sea. Waters draining from the Onondaga usually have high amounts of dissolved calcium, sulfur, and high electrical conductivity (NYS Museum, 1999).

Figures 3 and 4 illustrate the bedrock geology and topography of the area around Cranberry Bog in Greenwoods Conservancy, respectively.

![Figure 3](image_url) 

Figure 3. A map displaying the bedrock geology for the Greenwoods area and the locations of the wells sites and strike and dip sites. Elevation scale appears at the left side of the map.
Hydrologic Setting: The topography of the study area was caused by long term dissection of the Appalachian plateau by streams, and the action of glaciers advancing and receding over the area several times in the last few million years. This caused etching and burying of the pre-existing landscape. Several rock basins have been scoured into the uplands by the glaciers, forming the hollows and hills observed throughout Greenwoods. Cranberry Bog and other smaller water bodies in Greenwoods occupy these basins. One might expect that local groundwater flow is controlled by topography; flow moves from higher ridges into the valleys, and then into streams. However, this prediction of flow could be altered if vertical fractures are present, which would allow groundwater to move vertically along the fracture. The hypothesis that groundwater could be moving up from deeper aquifers to shallower aquifers and surface water forms the core of this study. Water derived from deeper geologic units, such as the Marcellus and Onondaga, should have distinctly different chemical signatures. This study evaluates these signatures by measuring
elemental concentrations and bulk parameters (electrical conductivity, total dissolved solids, salinity and pH) in surface water, shallow and deep aquifers and groundwater across Greenwoods Conservancy. Tables 1 and 2 summarize and describe the sampling locations.

Table 1. Summary of the location and elevation at each of the sampling sites.

<table>
<thead>
<tr>
<th>Location</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Elevation (masl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenwoods 1</td>
<td>42.71967</td>
<td>-75.08913</td>
<td>567.3</td>
</tr>
<tr>
<td>Greenwoods 2</td>
<td>42.71963</td>
<td>-75.08998</td>
<td>572.6</td>
</tr>
<tr>
<td>Greenwoods 4</td>
<td>42.71651</td>
<td>-75.08779</td>
<td>552.8</td>
</tr>
<tr>
<td>Greenwoods 5</td>
<td>42.71308</td>
<td>-75.10094</td>
<td>567.1</td>
</tr>
<tr>
<td>Well at Greenwoods 5</td>
<td>42.71249</td>
<td>-75.10022</td>
<td>577.2</td>
</tr>
<tr>
<td>Greenwoods 6</td>
<td>42.71256</td>
<td>-75.10045</td>
<td>579.3</td>
</tr>
<tr>
<td>Greenwoods 7</td>
<td>42.71254</td>
<td>-75.10981</td>
<td>567.8</td>
</tr>
<tr>
<td>Greenwoods 8</td>
<td>42.71117</td>
<td>-75.10586</td>
<td>569.5</td>
</tr>
<tr>
<td>Greenwoods 14</td>
<td>42.71104</td>
<td>-75.09547</td>
<td>555.0</td>
</tr>
<tr>
<td>Cranberry Bog South</td>
<td>42.71167</td>
<td>-75.09778</td>
<td>556.0</td>
</tr>
<tr>
<td>Cranberry Bog North</td>
<td>42.71875</td>
<td>-75.09604</td>
<td>551.3</td>
</tr>
</tbody>
</table>

Table 2. Attributes of the sampling sites.

<table>
<thead>
<tr>
<th>Dug Wells</th>
<th>Drilled Wells</th>
<th>Water Bodies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenwoods 2 (GW2)</td>
<td>Greenwoods 1 (GW1)</td>
<td>Cranberry Bog, South End (CBSE)</td>
</tr>
<tr>
<td>Greenwoods 4 (GW4)</td>
<td>Greenwoods 8 (GW8)</td>
<td>Cranberry Bog, North End (CBNE)</td>
</tr>
<tr>
<td>Greenwoods 6 (GW6)</td>
<td>Greenwoods 5 (GW5)</td>
<td></td>
</tr>
<tr>
<td>Greenwoods 7 (GW7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Greenwoods 14 (GW14)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Goals for the study: To identify fractures from linear trends on topographic maps and on the ground; to measure the water chemistry of shallow dug wells, deeper drilled wells and the bog; to identify spatial trends in water chemistry and characterize the bedrock associated with that water chemistry; to generate shallow groundwater flow path maps and to test the hypothesis that water is upwelling from deeper aquifers along regional fractures.
METHODS

Dug well sampling collection method:
Materials:
- Sampling pole and bottle
- 3 sample bottles
- HNO₃, used as a preservative for cation sampling
- 0.22 micron filter paper (See Figure 7)
- Vacuum filter, including hand pump, rubber hose that attaches hand pump to collection bottle, glass Buchner funnel that sample water is poured into to be filtered (see Figure 7)
- PCSTestr 35 Multi-Parameter Probe for temperature, pH, electrical conductivity
- Bucket
- Deionized (DI) water for rinsing the sampling bottles
- Duct tape/bottle labeling tape
- Sharpie
- Write-in-rain field guide book to record data
- Gas-powered pump to dewater wells, hose and gasoline
- Water-level indicator to determine depth to water table in wells

Steps for water sampling:
At each location, the sampling pole bottle, the top of the sampling pole, and the bucket were rinsed with deionized (DI) water. Water was collected from the site and used to rinse the bucket three times. The bucket was then filled with sample water, and tested with the multi parameter probe for electrical conductivity, total dissolved solids, salinity and pH (bulk chemical parameters.) After this, water was filtered through a vacuum filtration system (Buchner funnel and filter paper), and collected in a collection bottle (See Figures 5 and 6).

The vacuum filtered water was used to rinse the three sample bottles three times, filtered water was added to the sample bottle, along with several drops of HNO₃ to a pH < 2, which acts as a preservative to prevent microbial growth. Each bottle was labeled with date, time, location, presence of HNO₃, samplers, water body type, and unique identifier. Typically, 500 ml was collected for cation chemical analyses, and 500 ml collected for anions (sulfate, chloride) and nutrients. These samples were analyzed at the BFS lab for calcium, chloride, and alkalinity. Table 3 summarizes the methodologies for these, and all other, analyses.

Steps for pumping of dug wells:
Many of the wells in the monitoring program were shallow dug wells. While it seemed likely that groundwater was flowing through the well, to verify that the water was fresh from the surrounding aquifer, the drilled wells were purged. The following steps were followed:
- Extract a water sample, following procedures above.
- Measure the ground-to-water table depth using the water-level indicator tape measure.
- Insert hose pump all the way down the dug well and begin pumping.
Every 2 minutes re-measure and record the ground to water depth using the water-level indicator. Drain dug well completely.

Allow at least 24 hours before measuring groundwater level. Extract a water sample, following procedures above.

**Drilled well sampling collection method:**

Materials
- At least 3 sample bottles
- Bottle of HNO₃ preservative
- 0.22 micron Filter paper (See Figure 5)
- Filtration set-up, including hand pump, rubber hose that attaches hand pump to collection bottle, glass Buchner funnel that sample water is poured into to be filtered (see Figure 5)
- PCSTestr 35 Multi-Parameter Probe
- Bucket
- Gallon jug filled with deionized (DI) water
- Duct tape/bottle labeling tape
- Sharpie
- Write-in-rain field guide book to record data

Steps for collecting drilled well water samples:
The drilled wells were all located where a sink inside a cabin, or a faucet located outside, can be tested to get the parameters of the drilled well. Rinse bucket, multi-meter and vacuum filtration set-up materials with DI water.

The bucket that was used for testing was filled and rinsed three times with the sink/faucet water. The multimeter probe was placed into bucket with the conductivity/temperature setting on. The conductivity was recorded every minute until the conductivity and temperature began to stabilize. This typically took 10 to 15 minutes. The goal was to test the well water and not the water that has stagnantly been sitting in the pipes and could give unrepresentative results.

Once the temperature and conductivity stabilized, the bucket was emptied and allowed to refill. The multi-parameter probe was used to get the bulk parameters of conductivity, total dissolved solids, salinity, pH and temperature. This was done immediately, before the temperature of the water would rise. After this, the vacuum filtration was set up (displayed in Figure 5 and Figure 6). The vacuum was used to filtered water to rinse out the three sample bottles each three times. After rinsing, a water sample was collected in one bottle until it was half full. Then 11 drops of HNO₃ was added as a preservative. The bottle was capped, shaken and then filled the rest of the way with filtered water. The bottle was labeled “cations, 11 drops of HNO₃ preservative” and the designation of the well site, the date, the time, the samplers, and indicating it is a drilled well.

The remaining bottles were filled with the filtered water and labeled as “anions, general” along with the other labels stated above. These samples were analyzed at the BFS for calcium, chloride, and alkalinity (see Table 3).
Figure 5. Photo displaying, starting from top left and working towards bottom right; filter paper, Buchner funnel, filter, hand pump, rubber hose, collection bottle, pole sampling bottle.

Figure 6. Display of the vacuum filtration set-up with sampling bottles also shown.
Table 3. Summary of analytical chemistry methods.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Preservation</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Conductivity (µS/cm.)</td>
<td>None, Measured in field</td>
<td>Oakton PCS Testr 35 Multiparameter</td>
<td>Oakton Instruments; Eutech Instruments</td>
</tr>
<tr>
<td>Total Dissolved Solids (ppm.)</td>
<td>None, Measured in field</td>
<td>Oakton PCS Testr 35 Multiparameter</td>
<td>Oakton Instruments; Eutech Instruments</td>
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<tr>
<td>Salinity (ppm.)</td>
<td>None, Measured in field</td>
<td>Oakton PCS Testr 35 Multiparameter</td>
<td>Oakton Instruments; Eutech Instruments</td>
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<tr>
<td>pH</td>
<td>None, Measured in field</td>
<td>Oakton PCS Testr 35 Multiparameter</td>
<td>Oakton Instruments; Eutech Instruments</td>
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<tr>
<td>Temperature (°C)</td>
<td>None, Measured in field</td>
<td>Oakton PCS Testr 35 Multiparameter</td>
<td>Oakton Instruments;</td>
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<tr>
<td>Calcium (mg/L.)</td>
<td>Store at 4 °C</td>
<td>EDTA titrimetric method, 3500- Ca. D. Standard methods</td>
<td>APHA 1989</td>
</tr>
<tr>
<td>Chloride (mg/L.)</td>
<td>Store at 4 °C</td>
<td>Titrimetric mercuric nitrate method, 4500-Cl. C. Standard Methods</td>
<td>APHA 1989</td>
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</table>
Table 3 (cont.). Summary of analytical chemistry methods.

<table>
<thead>
<tr>
<th>Alkalinity (CaCO₃ mg/L.)</th>
<th>Store at 4 °C</th>
<th>Titrimetric sulfuric Acid Method, 820 HACW Test Kit-Model AL-DT</th>
<th>HACH Company</th>
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</thead>
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<tr>
<td>Alkalinity (CaCO₃ mg/L.)</td>
<td>Store at 4 °C</td>
<td>Titrimetric Method 2320 B. Standard Methods</td>
<td>APHA 1989</td>
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<tr>
<td>Total Phosphorous</td>
<td>H₂SO₄ to pH &lt; 2</td>
<td>Persulfate digestion followed by single reagent ascorbic acid</td>
<td>Liao and Marten 2001</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>H₂SO₄ to pH &lt; 2</td>
<td>Cadmium reduction method following peroxodisulfate digestion</td>
<td>Pritzlaff 2003; Ebina et al. 1983</td>
</tr>
<tr>
<td>Nitrate+ Nitrite</td>
<td>H₂SO₄ to pH &lt; 2</td>
<td>Cadmium reduction method</td>
<td>Pritzlaff 2003</td>
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<td>Ag, Al, As, B, Ba, Be, Bi, Ca, Ce, Co, Cd, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Ge, Hf, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pr, Rb, Re, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr</td>
<td>HNO₃ to pH &lt; 2</td>
<td>ICP-MS</td>
<td>Activation Laboratories Ltd.</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Geology: In order to study the regional fractures in the area, the orientation of the fractures were measured at two locations: at a bedrock outcrop of the Moscow formation located along Highway 80 north of Greenwoods (latitude: 42.72928 and longitude: -75.095779; displayed in Figure 9 as site 1) and along a stream where bedrock of the Moscow Formation was exposed (latitude: 42.71025 and longitude: -75.09826; displayed in Figure 9 as site 2 located just south of Cranberry Bog). These were the only two outcrops where fractures were readily visible and were suitable for accurate orientation measurements. The Moscow formation outcrop located along Highway 80 had a southside outcrop and a northside outcrop each situated on opposite sides of the road about 15 meters away from each other. Only fractures which were through-going, that is, cut through the entire section of rock, were measured.

We plotted the orientation data in a program called Open Stereo (Figures 7 and 8). This program creates projections called stereonets that show the orientations of planes in geographical space. Two directions are measured in the field which characterize the direction a plane is dipping and the magnitude of the dip. Directions are measured around the outside of the circle from 0 (North) to 360 in a clockwise fashion. The stereonet for the Highway 80 outcrop shows that the main regional fracture runs nearly north-south, with a second set of fractures that runs northeast to southwest (about 40-220 degrees) (Figure 7). The fractures along the stream appear to have the same orientation (Figure 8).

Figure 7. Display of a stereonet for the strike and dip values at the North End of Greenwoods, this Moscow formation outcrop is located right by highway 80. This represents site 1 in Figure 9.
Figure 8. Display of a stereonet for the strike and dip values along a stream, where the bedrock outcrops were located South of Cranberry Bog. This represents site 2 in Figure 9.

Cranberry Bog lies directly between the two fracture measurement locations, and aligns nearly perfectly with the north-south set of fractures. This suggests that erosional processes, such as rock quarrying by glaciers and preferential plucking of fractured blocks by streams, have taken advantage of the regional fracture system over geologic time to hollow out the depression in which Cranberry Bog rests.
Figure 9. Overview of the map locations for where the fracture measurements were taken. Site 1 represents the location of the highway 80 bedrock outcrop (see Figure 7). Site 2 represents the location of the stream bedrock outcrop (see Figure 8). The other dots indicate the location of wells and other water bodies tested.
**Hydrology:**

Since this project hinged on sampling surface and shallow groundwater, a significant question arises to what hydrologic conditions were like during the sampling period. Figure 10 below shows that April and May were a bit drier than normal, but June was substantially wetter, as reflected in the discharge in the Unadilla River, downstream from the Greenwoods watershed area. The data shows higher gage heights and larger discharge rates that were occurring while sampling for this project was taking place.

![Graph showing seasonal river flow compared to long term records on the Unadilla River at Rockdale, NY.](image)

Figure 10. Seasonal river flow compared to long term records on the Unadilla River at Rockdale, NY. Data and chart courtesy USGS [http://waterdata.usgs.gov/ny/nwis/uv?site_no=01502500](http://waterdata.usgs.gov/ny/nwis/uv?site_no=01502500).

One method to test the hypothesis of water upwelling from deeper aquifers along the regional fracture is to plot distance from regional fracture against the water chemistry parameters we tested for to see if there is a correlation. We measured electrical conductivity, pH, total dissolved solids, alkalinity and temperature. We also analyzed for a number of major and trace elements. Higher concentrations of barium and strontium in the water samples that are nearer to the fracture could indicate signs of deeper waters mixing with shallow groundwater as well.

Figures 11 through 19 plot the various parameters evaluated against the distance of the site to the regional fracture to identify potential correlation, which could indicate deep-water upwelling. Shallow groundwater flowlines, based upon contours, are proposed in Figure 20. Conductivity is presented in a map in Figure 21.
Electrical Conductivity:

![Electrical Conductivity vs Dist. from Regional Fracture](image1)

Figure 11. Conductivity versus distance from regional fracture. There is almost no correlation as the $R^2$ is 0.0001

Total Dissolved Solids:

![T.D.S vs. Distance from Regional Fracture](image2)

Figure 12. T.D.S versus Distance from regional fracture. There is almost no correlation as the $R^2$ is 0.0097
Salinity:

Figure 13. Salinity versus distance from regional fracture. There is almost no correlation as $R^2$ is 0.0173.

Salinity is very important to evaluate when testing the hypothesis of deeper aquifer waters entering into shallow aquifers via a large regional fracture. Due to the Moscow formation and other shale formations in this region of New York forming in a deep ocean environment, they tend to exhibit high salinity concentrations because they form deep aquifer brines. This means that if we were to see higher salinity values for water bodies closer to the regional fracture, then the deep aquifer brines high in salinity have been making their way to shallower aquifers via the distance from the regional fracture. There being little correlation, we can deduct that the regional fracture is having little influence on deeper high in saline brines make their way to shallower waters.

pH:

Figure 14. pH versus Distance from regional fracture. There is almost no correlation as $R^2$ is 0.0251.
Calcium:

Figure 15. Calcium vs. Distance from regional fracture. There is little to no correlation as $R^2$ is 0.1243.

Alkalinity:

Figure 16. Alkalinity vs Distance from regional fracture. Almost no correlation is found as the $R^2$ value is 0.047.
Temperature:

Figure 17. Temperature vs Distance from regional fracture. The correlation is very low with an $R^2$ value of 0.2699. Though this is a low correlation, it is higher than any of the other parameters tested in this study. As you can see the water samples taken further away from the regional fracture appear to be lower in temperature, but this is due to the fact that surface and groundwater data are included in the above diagram, and the highest temperatures are in Cranberry Bog during the height of summer.

Barium:

Figure 18. Barium vs Distance from the regional Fracture, the correlation is almost none as the $R^2$ value is 0.0368.
Figure 19. Strontium vs Distance from the regional Fracture, the correlation is little to none as the $R^2$ value is 0.0069.
Figure 20. This map displays shallow groundwater flow paths. This map was generated in Google Fusion with 40 meter contours.
Figure 21. Map summarizing electrical conductivity. The small dots are representative of sample sites with electrical conductivity (E.C) of 0 to 100 μS/cm. The squares represent an E.C of 100 to 200 μS/cm, the triangles represent an E.C of 200 to 300 μS/cm, and the circular symbol with a dot inside it represents 300 to 400 μS/cm. The line going through the middle of the map represents the regional fracture in Greenwoods. This helps to disprove the theory of the regional fracture allowing deeper aquifer waters reaching the surface, because deeper aquifer waters tend to have higher electrical conductivity. This means if the theory was true, we would see higher electrical conductivity along the regional fracture line. This does not appear to the case as 3 to 4 of the small dots representing E.C.s of 0 to 100 fall along this line.

Hydrology and Geology: This section is a comparison of the sampled water bodies that are in contact with the glacial till (such as the dug wells, streams and bog) and the sampled water bodies that are in contact with the Moscow formations.
Upon viewing Figure 21, one can conclude that the water-rock relations of the Moscow formation are creating environments that allow for higher elemental concentrations than those in the glacial till water-rock relations. The glacial till water bodies are all at lesser depths than the Moscow formation water bodies. Most of the Moscow formation water bodies are drilled wells that penetrate to about 50 meters depth, whereas the glacial till water bodies are all within 10 meters depth as the dug wells do not go as deep. Upon viewing the visual above it appears (with the exception of chloride, which was in very small concentrations) that the higher elemental concentrations remain in the lower aquifer as these values were repeatedly taken from the same well sites. It also appears that the lower conductivity of the glacial till is allowing water to move quicker not allowing stagnant water to accumulate higher element concentrations. The Moscow formation water is not moving as fast and higher elemental concentrations are existing in these waters.

Lastly, Figure 23 compares the elemental concentrations and electrical conductivities in lakes, streams, and wells at Greenwoods Conservancy. The stagnant waters in the wells appears to be in higher elemental concentrations and higher in electrical conductivity than the quicker moving and lower water residence times of the stream and lake.
Figure 21. A display of the concentrations of strontium, barium, calcium, chloride, and electrical conductivity for water bodies located in glacial till vs the Moscow formation.
CONCLUSIONS

We find no correlation between well proximity to regional fractures and well chemistry (Figures 14 to 22.) Presence of ponds and bogs in upland regions implies low conductivity and/or high water tables. Zones of deep groundwater discharge at the surface are highly unlikely, especially in upland regions which serve as recharge zones. Water chemistry of Cranberry Bog is consistent with local shallow water wells and rules out groundwater discharge into the bog from deeper groundwater flowing up along a regional fracture zone.
Comparing the flowlines data with the electrical conductivity map and the glacial till elemental concentrations with the Moscow formation elemental concentrations, one can conclude that the flowlines do not have as great of an influence on elemental concentrations in water bodies than the water rock relations do (Figures 20 and 21.) The water rock relations have a much greater influence because the Moscow formation water rock relations were higher in most elemental concentrations (Figure 22)

REFERENCES


