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Chloride Monitoring at Coldwater Spring

Sophie M. Kasahara
Earth Sciences Department
University of Minnesota, Twin Cities
Minneapolis, Minnesota 55455 USA

Faculty Advisor: Professor E. Calvin Alexander, Jr.

Abstract

Coldwater Spring in Minneapolis, Minnesota was the original water supply for Fort Snelling in the 1840s; is a sacred spring to Native Americans and is now part of the National Park System. This project monitored the changes in salinity levels at Coldwater Spring to document human impacts on the spring's water quality. Weekly testing for temperature, dissolved oxygen, conductivity, pH and anion levels, and monthly analyzing for cation and alkalinity levels were conducted at Coldwater Spring and the adjacent Wetland A from February 2013 through April 2014. Coldwater Spring is classified as a gravity spring in which the spring's water is supplied from recharge areas and travels through a permeable surface until it hits an impermeable surface that does not allow it to travel further into the ground. Coldwater Spring's water flows through fractures in Platteville Limestone of Ordovician age. Studies on this formation have shown that it is ineffective at filtering out many of the contaminants from the recharge areas, in this case residential housing and major highways. The basic chemistry of Coldwater Spring is the calcium magnesium bicarbonate water typical of carbonate springs. However, on an equivalent basis Coldwater Spring's water currently contains almost as much sodium as calcium + magnesium and more chloride than bicarbonate. In 1880, a study conducted of Coldwater Spring by Army Captain Maguire found the chloride levels to be about 4.5 ppm. During the current study the chloride content in the spring fluctuated smoothly from about 320 ppm from March 2013 climbed to a maximum of 430 ppm in June 2013 and declined to 340 ppm in September 2013 and then rose slowly to 385 ppm in April 2014. These levels are about 100 times the levels from 1880. This major anthropogenic sodium chloride component has a chloride to bromide ratio of 2500 ± 300, well within the range of chloride to bromide ratios of road salt, 1,000 to 10,000. Road salt is applied to two major multi-lane highways close to the spring throughout the late fall, winter and early spring. The several month delay in the peak salt concentration appears to be a travel time delay between the surface application and the spring. The temperature of Coldwater Spring decreased smoothly from 12.7 °C in February to 11.2 °C in May and then increased to 13.0 °C by late November. This is not a temperature constant spring. The peak in the spring's temperature is delayed by about six months from the air temperature pattern. The normal temperature of a spring in this area is about 8 °C, so the higher temperatures of the spring also indicate an outside source, such as underground utilities, that may be heating the spring. The water also contains a significant nitrate-nitrogen component of 2.9 ± 0.3 ppm, which is additional evidence of anthropogenic impact.

Keywords: Karst Spring, Chloride, Temperature

1. Introduction:

In the Twin Cities Metropolitan area (TCMA), roughly 350,000 tons of de-icing road salts are applied to the TCMA roads every year[1]. The majority of this salt dissolves in snow-melt runoff that either soaks into the groundwater and contaminates wells and springs, or flows into ditches, sewers and waterways that lead to lakes, streams, and rivers. According to a recent study conducted by Heinz Stefan's group, about 70% of the road salt applied in the Twin Cities area stays in the regions' watershed[2]. The road salt used is about 60% chloride and 40% a positive ion,

usually sodium, and is generically referred to as NaCl[3]. This road salt run-off can lead to high levels of salinity in freshwater areas due to the NaCl dissolving in the water[4]. This is enormously harmful to freshwater aquatic life, regional mammals and birds, and plants native to Minnesota.

This project monitored the water quality in Coldwater Spring, Minneapolis, Minnesota, to evaluate the impact of anthropogenic pollutants on the spring and an adjacent wetland.

1.1. Salinity Effects On Wildlife

Ten percent of freshwater species can die off after just 30 days at salinity concentrations of 220-240 (mg/L), trout behavior is affected at levels as low as 250 (mg/L), and the overall diversity of aquatic species decreases as the salinity concentration rises[3]. According to the Minnesota Pollution Control Agency's 2010 draft report, 11 metro-area streams have levels of chloride concentration above 230 (mg/L)[5]. Salinity in fresh-water sources also causes deer and moose, who drink the water, to be less afraid of humans and automobiles, and birds, such as sparrows, can die after eating only two salt particles. Plants as far as 200 feet away from the roadside can still be affected by the rise in salinity, and just a 30 mg/L concentration can lead to damage to coniferous species such as the pine tree[3]. Because groundwater is the source for drinking wells, high levels of salinity can also affect humans on restricted-sodium diets[2].

1.2. Background On The Sample Sites

Coldwater Spring is classified as a gravity spring in which the spring's water is supplied from recharge areas and travels through a permeable surface until it hits an impermeable surface that does not allow it to travel further into the ground[6]. Coldwater Spring's water flows through fractures in Platteville Limestone of Ordovician age. Studies on this formation have shown that it is ineffective at filtering out many of the contaminants from the recharge areas, in this case residential housing and major highways[7].

Coldwater Spring has a very interesting historical background, being that it is the largest free-flowing spring in Minneapolis. Coldwater Spring is an important Native American cultural site[6] and is an integral part of the history of Fort Snelling and Minneapolis. The spring is now a part of the National Park Service's Mississippi River National River and Recreation Area[7] and is open to the public. Although the NPS and MDH agree that the water is not potable, it is clear that numerous individuals and groups collect the spring water to drink.

The Wetland A sample site was previously a building owned by the Bureau of Mines: Twin Cities Research Center. The buildings were closed in 1996 and all but the historic springhouse and reservoir were taken down by February 2012 during the restoration of Camp Coldwater Spring as a National Park[7].

2. Methodology

Weekly visits were conducted to Coldwater Spring and Wetland A to record the temperature, measure the conductivity, dissolved oxygen and pH levels of the spring using a Thermo Orion multi-meter. Also obtained were weekly anion samples. The anion samples were analyzed using ion chromatography. Samples were collected monthly for alkalinity analyses (by digital titration methods) and cation analyses (ICP/MS methods) of the water. Water samples were collected from the two sites from the beginning of February 2013 to the end of April 2014. The timing of this data yielded a measure of the rise and fall of the springs' salinity levels as the snow is melting and the salt is washing into and through the groundwater for a full year.

3. Data and Conclusions

Although Coldwater Spring and Wetland A are less than 100 meters apart, their water chemistries and flow rates are significantly different.

3.1. Chloride Levels

The chloride concentrations in Coldwater Spring and Wetland A (figure 1) showed high and variable chloride concentrations.

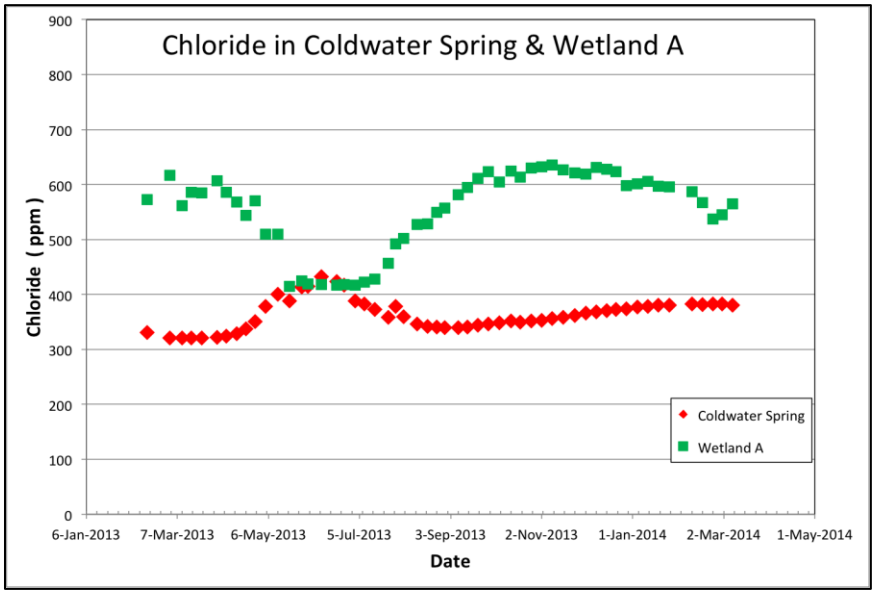

Figure 1. Displays the chloride levels in Coldwater Spring and Wetland A, measured weekly for a little over a year.

Figure 1 displays the weekly chloride levels at both sample sites for about a year. The chloride levels were measured in the Earth Science Department, University of Minnesota, using ion chromatography.

3.1.1. historical data on the chloride levels in Coldwater Spring

In 1880[8], a study conducted by Army Captain Maguire reported the chloride level in Coldwater Spring to be 0.26 grains per gallon which is equivalent to 4.5 ppm in modern units.

3.1.2. chloride levels in Coldwater Spring

Between February 2013 and April 2014, the chloride content in the spring fluctuated smoothly from about 320 ppm in March, climbed to a maximum of 430 ppm in June and declined to 340 ppm in September. These levels are about 100 times the levels from 1880. The chloride levels are at their highest level throughout a roughly four-month period, which is about the same amount of time road salt would be applied to Minnesota roads. Ignoring the chloride increase over the winter months, chloride levels still appear to be increasing steadily. Road salt is applied to two major multi-lane highways close to the spring throughout the late fall, winter and early spring. The several month delay in the peak salt concentration appears to be some sort of travel time delay between the surface application and the spring.

3.1.3. chloride levels in Wetland A

Wetland A chloride levels (figure 1) were higher than the chloride levels at Coldwater Spring, and displayed an inverse relationship to Coldwater Spring. The Wetland A chloride concentrations started at about 620 ppm at the beginning of March 2013 and fluctuated smoothly down to a minimum of 420 ppm by the end of May 2013 and then

increased smoothly back up to 620 ppm by the end of September 2013. The high chloride levels are also linked to the road salt being applied on the roads around the spring, but the reason for the mirror image trend in the chloride levels is unknown. The chloride levels in Wetland A are over 100 times the original 1880 chloride level of 4.5 ppm in Coldwater Spring.

3.2. Chloride/Bromide Mass Ratios

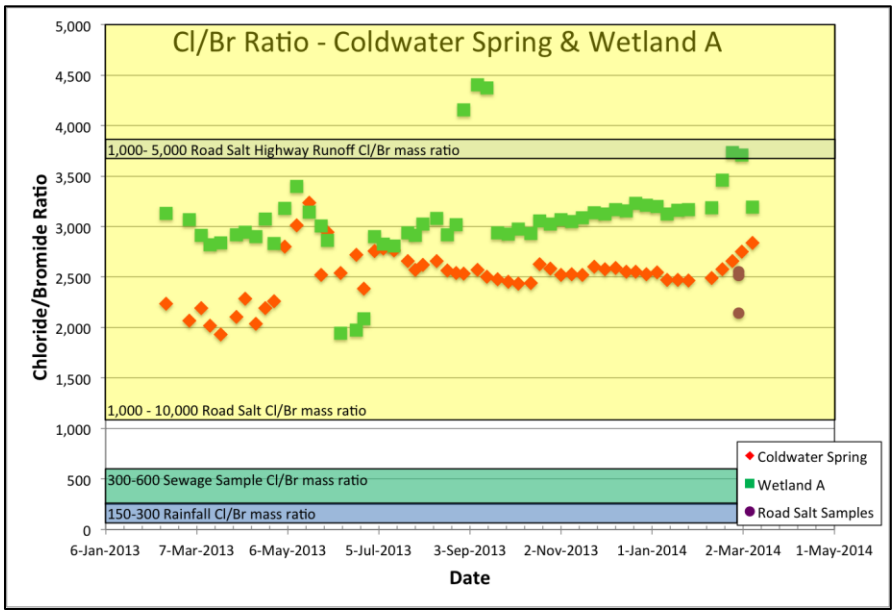

Figure 2. Displays the chloride to bromide mass ratios for Coldwater Spring and Wetland A, calculated weekly for a little over a year, and for three road salt samples taken from different sites on the University of Minnesota campus.

Salt from different sources has different, characteristic chloride to bromide ratios[9]. Measurement of the chloride to bromide ratios in Coldwater Spring and Wetland A helps to identify the source of the salt. Figure 2 displays the weekly chloride to bromide mass ratios from both sample sites for about a year. It also displays the chloride to bromide mass ratio of three road salt samples taken from different sites on the University of Minnesota campus. The chloride and bromide levels were measured in the Earth Science Department, University of Minnesota, using ion chromatography.

3.2.1. chloride/bromide mass ratios in Coldwater Spring and Wetland A

The chloride to bromide ratios in both sample sites were well within the range in which road salt is the primary source. These ratios also fall in line with the three samples of road salt taken at three different sites around the University of Minnesota campus. Both of these observations imply that road salt is the primary contributor to the high chloride levels in Coldwater Spring and Wetland A.

3.3. Temperature

3.3.1 historical temperature data about Coldwater Spring

In 1836 and 1837, a French explorer by the name of Joseph Nicollet measured the temperature of Coldwater Spring in both the summer and the winter months[10]. He quotes about Coldwater Spring's temperature:

"Of the numerous springs that issue from the foot of the…bluffs [adjoining Fort Snelling] there is one particularly deserving of notice. It is very abundant and perfectly shaded. It goes by the name of Baker's spring. Having taken its temperature three times a day during twenty days of the month of July, 1836, and then again during the following winter months, I never found it to vary more than 46°F in July, and 45.5°F in January."

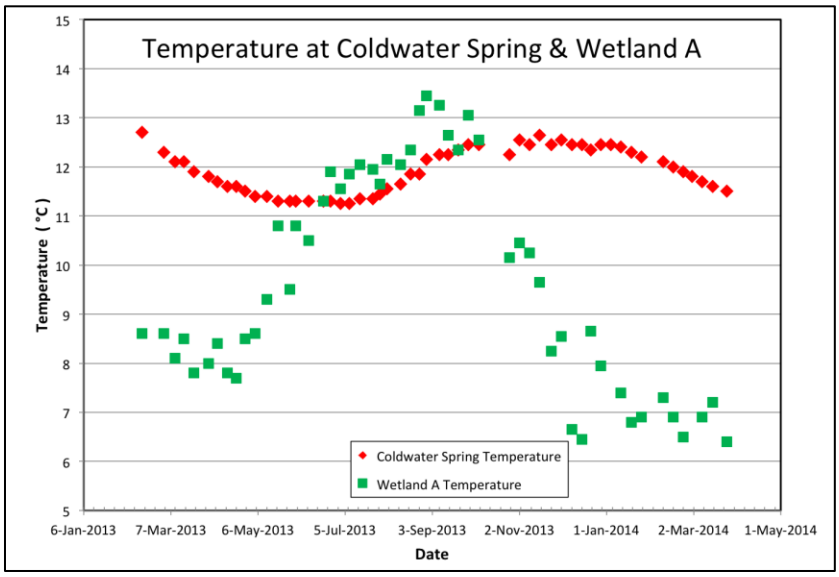

Figure 3. Displays the temperature levels in Coldwater Spring and Wetland A, measured weekly for a little over a year.

Figure 3 displays the weekly temperature of Coldwater Spring and Wetland A from February 2013 through April 2014. The temperature was measured using an ASTM calibrated thermometer.

Converting the temperatures from Fahrenheit to degrees centigrade, the measured temperature average of Coldwater Spring was about 7.8°C in July and 7.5°C in the winter. This indicates that in the summer of 1836 and the winter of 1837, Coldwater Spring's temperature was essentially constant. The temperature of gravity springs is typically the average annual air temperature of that region. The shallow groundwater temperature in this part of Minnesota is about 8°C.

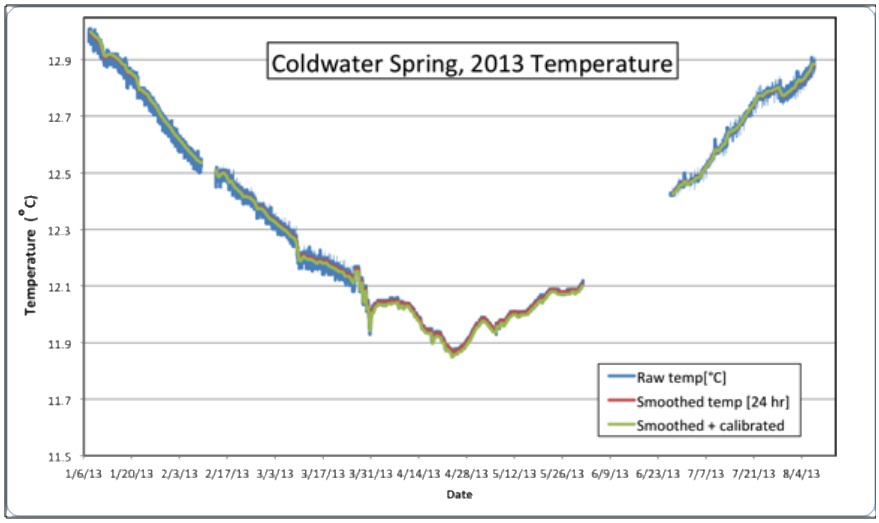

Figure 4. Displays the temperature levels in Coldwater Spring, measured every 15 minutes for about seven months.

Figure 4 displays the temperature of Coldwater Spring measured in increments of 15 minutes for roughly seven months. The temperature was measured using a data logger that was placed at the head of the spring.

3.3.2. temperature in Coldwater Spring

In 2013 and 2014, the field thermometer temperature of Coldwater Spring (figure 3) fluctuated between 11 and 13 degrees centigrade. This is a 3 to 5 degree increase from the 1836 and 1837 temperature levels. Since the temperature fluctuates by about two degrees, it is clear that Coldwater Spring is no longer a constant temperature spring. The lowest point in the temperature fluctuation occurs in early June, which indicates a six-month time delay between the spring water and the air temperature.

To account for the springs significant rise in temperature, the spring likely has an underground heat source such as the heat from the parking lot or underground utilities. The data logger temperature (figure 4) varies a little from the thermometer obtained temperature, with a minimum of about 11.9 degrees centigrade that occurs at the end of April. The data logger also indicates that there is not a direct way for rainwater to get into the spring. If there were a direct source of rainwater, the data logger graph would show cold spikes downward in the winter, and warm spikes upward in the summer.

3.3.3. temperature in Wetland A

Coldwater Wetland A thermometer temperatures ranged between 6 and 14 degrees centigrade, with the temperature peaking at the end of August. This indicates that Wetland A is also not a constant temperature spring, and that the groundwater temperature was delayed from the air temperature by about two months. Wetland A temperatures did dip low enough to reach the average spring temperature of 8 degrees centigrade, so an underground heat source is not required to explain this wetland's temperatures.

3.4. Nitrate-Nitrogen Levels

According to the 1974 Safe Drinking Water Act, the maximum contaminant level goal (MCLG) for nitrate is 10 ppm[11]. Although the nitrate levels in each sample site is significantly below this drinking standard, maximum contaminant levels are purposely set as close as possible to the health goals. Therefore the levels found in Coldwater Spring and Wetland A are still significantly high, indicating a source of pollution such as lawn fertilizer run-off or a broken sewage line.

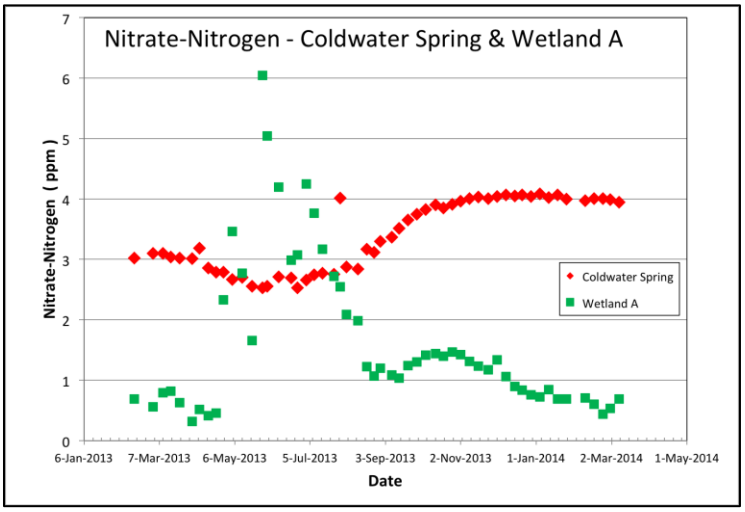

Figure 5. Displays the nitrate-nitrogen levels in Coldwater Spring and Wetland A, measured weekly for a little over a year.

Figure 5 displays the weekly nitrate-nitrogen levels in Coldwater Spring and Weltand A, measured from February 2013 through April 2014. The nitrate levels were measured in the Earth Science Department, University of Minnesota, using ion chromatography.

3.4.1. nitrate-nitrogen levels in Coldwater Spring

The nitrate-nitrogen levels in Coldwater Spring (figure 5) varied between about 2.5 ppm to 4 ppm. The values started at around 3.1 ppm in March 2013 fluctuated smoothly down to a minimum of 2.5 ppm in May 2013 and then climbed back up to a steady maximum of 4 ppm in November 2013. This trend is opposite to the chloride trend (figure 1) because the lowest points on the nitrate-nitrogen graph occur almost simultaneously with the highest points on the chloride graph. The Coldwater Spring nitrate-nitrogen graph also had an inverted relationship to the Wetland A nitrate-nitrogen graph, just as the Coldwater Spring and Wetland A chloride graphs had an inverse relationship.

3.4.2. nitrate-nitrogen levels in Wetland A

Wetland A had a wider nitrate-nitrogen level range than Coldwater Spring, varying between about 0.5 ppm and 6.0 ppm. The nitrate-nitrogen level started low for Wetland A at around 0.5 ppm in March 2013 and April 2013, increased at the end of May 2013 reaching its maximum at about 6.0 ppm, and then decreased in July 2013 and August 2013 back to around 1.2 ppm in mid-August. The Wetland A nitrate-nitrogen level increased again about a month later in September 2013 for another smooth fluctuation in which it reached a maximum of 1.5 ppm at the end of October 2013 and then decreased back down to 0.7 ppm at the end of January 2014.

3.5. Water Flow Monitoring

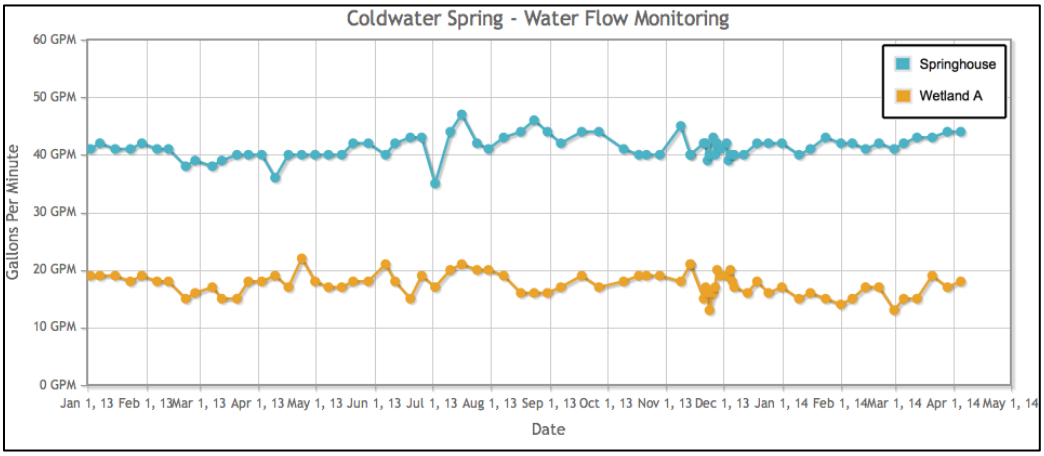

Figure 6. Displays the water flow rates in Coldwater Spring and Wetland A, measured weekly for roughly a year and a half. Data from (http://www.rangeroncall.com/misc/coldwater/flowdata/index.html).

Figure 6 shows the weekly water flow rates in Coldwater Spring and Wetland A, measured for roughly a year and a half by the National Park Service.

3.5.1. water flow monitoring in Coldwater Spring

The first observation about the water flow is that Coldwater Spring flows at about twice the rate as Wetland A. Another observation is that the flow rates are very constant, except for a slightly negative slope seen in Wetland A. This indicates that the flow in both springs does not account for the large chloride and nitrate concentration fluctuations.

3.6. Three Dimensional Piper Diagram

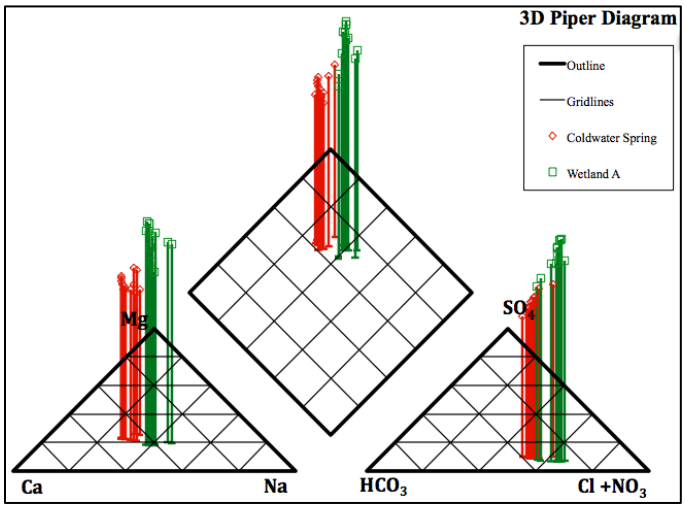

Figure 7. Displays the major ion water chemistries of Coldwater Spring (in red) and Wetland A (in green) on a 3-D Piper Diagram.

3.6.1. three dimensional piper diagram of Coldwater Spring

The 3-D Piper Diagram (Piper, 1944, figure 7) compares water chemistry of the Coldwater Spring and Wetland A monthly samples. Piper Diagrams are a graphical technique for displaying and interpreting the major ion chemistries of water samples[12]. The lower left triangle is a ternary diagram of the major dissolved cations. The lower right triangle is a ternary diagram of the major anions. And both of these are projected into the middle square. The total concentrations of the dissolved ions are shown by the vertical bars.

The large concentrations of chloride are not balanced by the sodium concentrations. This indicates that ion exchange occurred between the applications of the road salt, and when the road salt infiltrates the spring. The abundance of calcium and magnesium may also result from the recharge water passing through Platteville Limestone of Ordovician age[13]. Solution of the Platteville produces calcium, magnesium and bicarbonate ions. Most springs from carbonate rocks in Minnesota fall closer to the bicarbonate corner of the anion triangle than to Coldwater and Wetland A. The displacement of the Coldwater Spring and Wetland A data toward the chloride plus nitrate corner is a measure of the large salt and nitrate contamination of the spring and wetland.

4. Summary and Conclusions

Coldwater Spring and the adjacent Wetland A are heavily impacted by road salt spread on the adjacent major highways. The chloride levels in Coldwater Spring are about 100 times larger than were present in the 1880s before the use of deicing road salt. The temperature of Coldwater Spring is variable and has increased about 5 °C since the early 1800s. The nitrate levels in Coldwater Spring are elevated but not yet to the drinking water standard. All three of these observations indicate a major impact on Coldwater Springs' water quality by human activities in the recharge area feeding water to the spring.

5. Acknowledgements

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