

WINTERTIME CATION AND CONDUCTIVITY ANALYSIS OF THE CANNON RIVER



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INTRODUCTION

The Cannon River is a tributary to the Mississippi that flows through southern Minnesota. Located in Rice country, the river drains a watershed of 3,780 km² (about 1,460 mi²) containing several springs which flow from the Shakopee aquifer. The river flows through a primarily rural-agrarian region through a river valley comprised of sedimentary rocks such as dolomite and sandstone. Its path takes it through Northfield Minnesota, home to Carleton College, making it a frequent subject of study for students. In the last two years, two groups of students have focused on properties such as anion and cation concentration, CFCs, amount of dissolved oxygen, and turbidity. Specifically, tests have been run to determine the amounts of different cations such as potassium, magnesium, ammonium, sodium, and calcium while also monitoring the temperature and conductivity. We build on previous information and analyze it with regards to the seasonal variance of river quality.

While many studies have isolated these individual factors there has been a lack of focus concerning how they vary over time. Unlike studies in the past, measurements taken in this experiment were recorded during the winter season as opposed to during the spring or fall. We also monitor the conductivity at the different sites, which provides information about the water quality. Since runoff attributed to farming occurs primarily during the fall and spring seasons, higher levels of cations should be found in those periods than during the winter season and the observed water quality in this experiment should be in exceptional condition.

Our study provides a basis upon which to contrast the findings of previous and future groups during the fall and spring seasons. Measurements that were taken at the

five different sites will allow the fluctuations that take place in water quality to be seen clearly throughout a greater part of the year. See Appendix C for a map of our sampling locations.

PREVIOUS WORKS

A number of students at Carleton College have studied the Cannon River in some depth for the past few years. Specifically, we have used the study performed by advanced geology students in March 2004, and studies performed by beginning (environmental) geology students from the falls of 2004 and 2005. In all cases, the rivers were found to be generally healthy and significant discussion explored the meanings of various analyses.

The Environmental Geology students tested, very similarly to us, for the seven anions (Bromide, Phosphate, Sulfate, Chloride, Fluoride, Nitrate, and Nitrate), and sometimes cations (specifically Calcium). They also tested for conductivity, temperature, salinity, and dissolved oxygen. Their experiences and experiments were very similar to ours, except that their samples were taken in September and October, contrasting our winter sampling. Additionally, each group in these classes focused more narrowly on a specific tributary or region of the Cannon, whereas our study serves to get a broader look at the various tributaries of the Cannon all at once. Their findings are summarized in Table 1.2.

An investigation from fall of 2005 into the Cannon River's springs also provides useful data. Using analysis of the ion composition of the water, the investigation concluded that the anion most rapidly deposited into the Cannon River is sulfate, at a

discharge rate of 75.764 mg/s at one site and 465.26 mg/s at another. The most rapidly deposited cation was found to be calcium. This gives us a little insight into the chemical makeup of the river, which will be useful in examining any changes or new patterns that may have occurred in that area. It is unclear if the problems observed in this study are unique to the springs or if they extend to the rivers as well. Our analysis did not explore this further. The study concluded by recommending a further investigation into the presence of cation, sediment, and heavy metal loads of the Cannon River and its affiliate bodies. We may be able to provide insight into these areas given our more direct analysis of the makeup of the river itself.

The March 2004 geology study examined groundwaters of the Prarie-du-Chien Aquifer. They sampled wells and springs, and analyzed at many more cations. They also were able to look at the stable isotope concentrations. Their findings are summarized, along with some of their research, in Table 1.1

Due to our project's goal of examining the health of the Cannon in the winter compared to what we know to be true over a longer range of time, these data prove to be very significant.

In addition, there have been other experiments previously performed in relevant areas of the Cannon River watershed that analyzed similar aspects of water quality. *Geomorphology and Water Quality of Prairie Creek in Nerstrand Big Woods State Park, Minnesota* by Eleanor Bartolomeo, Adam Myers and Nicklaus Welty examined Prairie Creek which is located in the Rice and Goodhue counties. Among the substances sampled were nitrate, phosphate, and sulfate. In the section of the Prarie Creek which was examined they found nitrate and nitrite levels to be below average with

the exception of the samples taken under a bridge near a construction site. Within one of the sites they recorded orthophosphate levels that exceeded the EPA limit by a factor of ten.

Nitrogen and Phosphorus in Steams in Part of the Upper Mississippi River Basin, Minnesota and Wisconsin, 1984-93 by S.E. Kroening focused on determining the nitrogen and phosphorus levels in different Minnesotan rivers. It notes the relatively high concentration of phosphate and nitrate in the Cannon and other rivers surrounded by agricultural areas. At many of the samples sources, levels of phosphorus exceeded the recommended level of .1mg/L, including parts of the Cannon River.

In *Geomorphology, Geochemistry and Soil Erosion Along an Agricultural Stream* by Kristina Brady, Kristen Iriarte, and Dan Leistra, a small section of Prairie Creek was analyzed in order to determine the effect of riparian buffers on water quality. Among the different tests for water quality were pH, dissolved oxygen, salinity, temperature, turbidity, and conductivity. The water samples were also analyzed to determine the presence of certain anions. The amount of nitrate they measured at different parts of the stream varied from 12mg/L to 24mg/L. The phosphate readings were from .36mg/L to .88mg/L.

METHODS

Measurements were recorded from late January throughout February 2006. Water samples were taken from five separate sites- Faribault, Rice Creek, Wolf Creek, Hwy. 3 Mile 5 on the Cannon River, and Heath Creek. A total of three samples were collected from each site, with the exception of the Faribault site, which was not recorded during the first round of sampling. A YSI meter was also used to measure the salinity, temperature, and conductivity of the water. It was used in order to provide information as to the amount of dissolved nutrients present in the water. Samples were analyzed by an ion chromatograph to detect levels of anions and cations, specifically the amount of magnesium, potassium, calcium, sodium, and ammonium. Our initial intent was to test for anions such as sulfate, bromide, nitrate, and phosphate, but due to a malfunction of the atomic absorption spectrometer we were unable to attain this particular set of data.

RESULTS

Conductivity

The results we obtained for conductivity were fairly consistent at the Northfield Cannon River site, Heath Creek, and Rice Creek; excluding one low value (232.5 μ s) from the Northfield site on Feb. 8, these values ranged from 339 to 380 μ s. Values were higher at the Faribault site, at 421.1 and 474 μ s. Wolf Creek had lower values, ranging from 255.1 to 305.1 μ s. The averaged conductivity value is 348.7 μ s. See Figure One below.

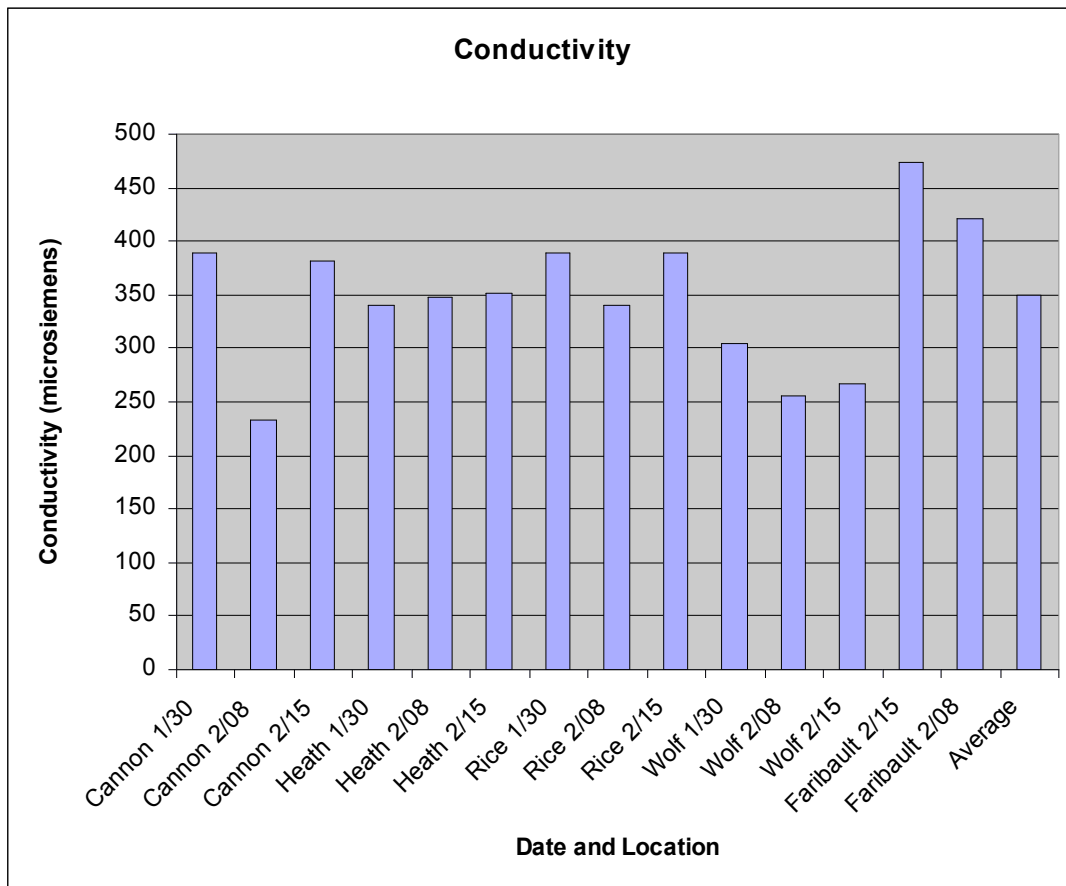


Fig. 1: Conductivity by date and location

Temperature

The highest recorded temperature recorded in this study was 3.5° taken at Rice Creek. The lowest temperature was 0.0° recorded at Heath Creek on February 8 and again on February 15. The average temperature is 1.1°. All temperature recordings are in degrees Celcius. The weather was fairly mild for a Minnesota February when we were taking these readings; all of our testing days were sunny. See Figure Two below.

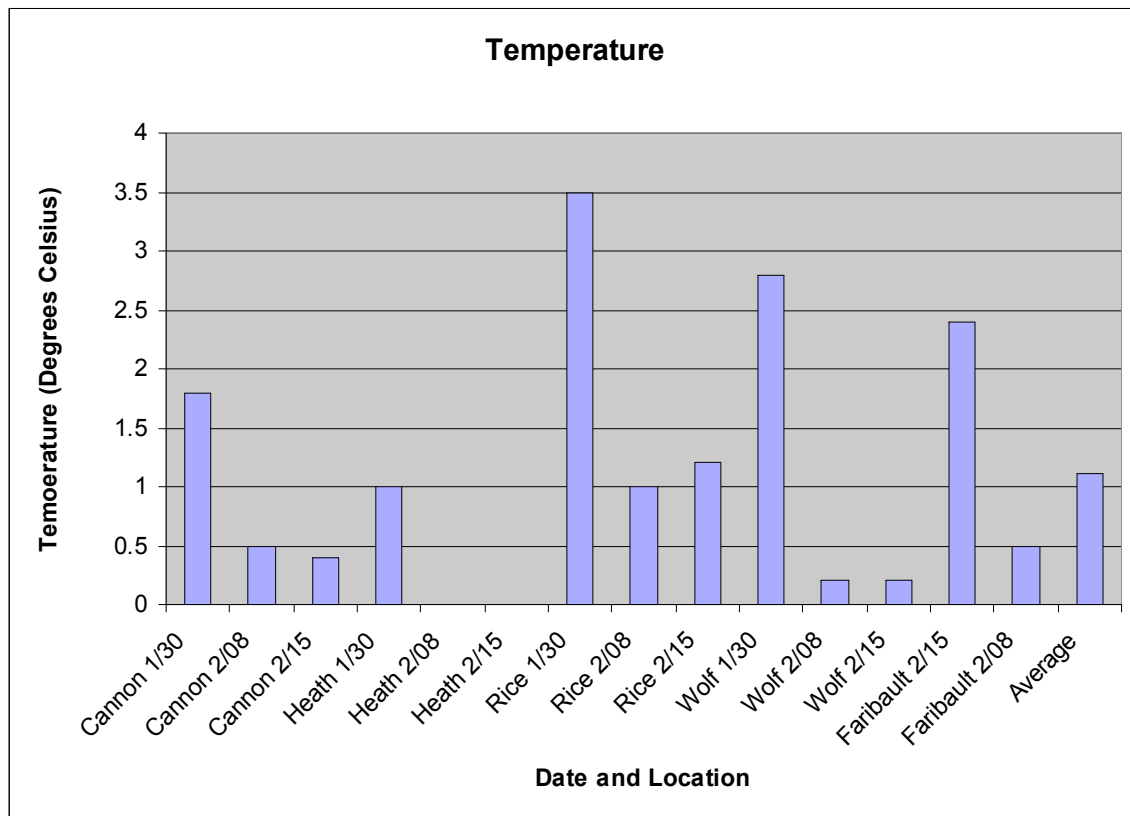


Fig. 2: Temperature by date and location

Ammonium

Ammonium levels were extremely low in all of the places we sampled; each sample location had zero ammonium at least once. Our highest recorded value was from the Heath Creek sample on January 30, at a level of 3.63 mg/L. The average ammonium level in our waters is 0.95 mg/L, although no ammonium showed up in four of eleven samples. See Figure 4; for complete results, see Appendix B.

Calcium

The levels of calcium in the Cannon River and its tributaries were, with one exception, between 50 and 80 mg/L. The sample from Rice Creek on February 15 yielded a measurement of 86.46 mg/L. The lowest measurement, 51.17 mg/L, also came from a February 15 sample taken at Wolf Creek. Our average calcium result was 68.50 mg/L, and the average is a good representation of what we found. Calcium was the most prevalent of any of the cations we tested. See Figure 3; for complete results, see Appendix B.

Magnesium

Magnesium levels ranged from the lowest at Wolf Creek, at a concentration of 40.96 mg/L, to the highest at Rice Creek, at a concentration of 66.25 mg/L. Both samples were taken on February 15. There was fluctuation within this range, but the average value is 54.31 mg/L. See Figure 3; for complete results, see Appendix B.

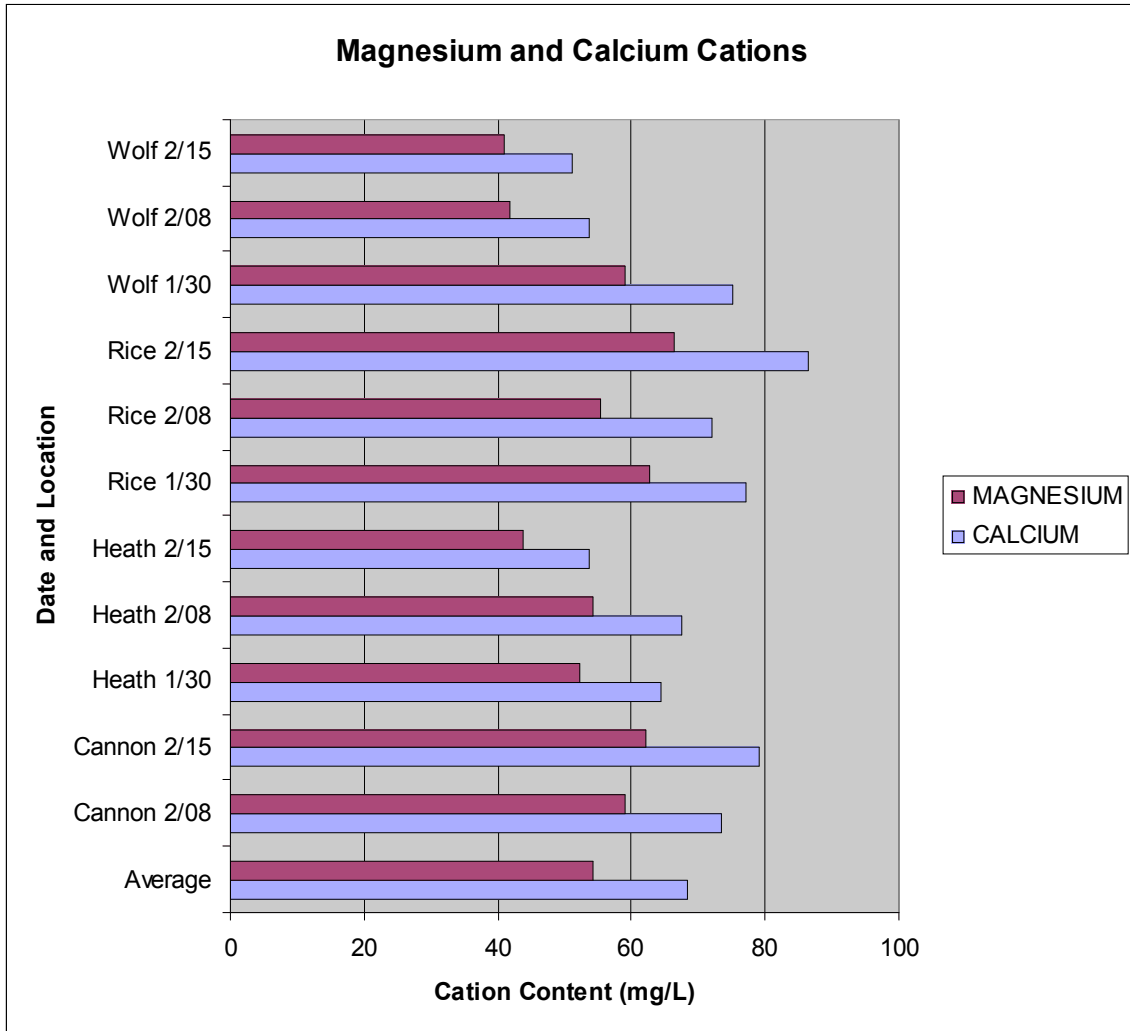


Fig. 3: Magnesium and Calcium cation results by date and location

Potassium

Our potassium levels ranged from 6.89 mg/L at the Northfield Cannon River site on February 15, to 24.45 mg/L at Heath Creek on January 30. Potassium was present in all samples. Heath Creek had higher levels, and Rice Creek had lower levels; Wolf Creek and the Northfield Cannon sites, with one exception, were closer to the average value of 15.57 mg/L. See Figure 4; for complete results, see Appendix B.

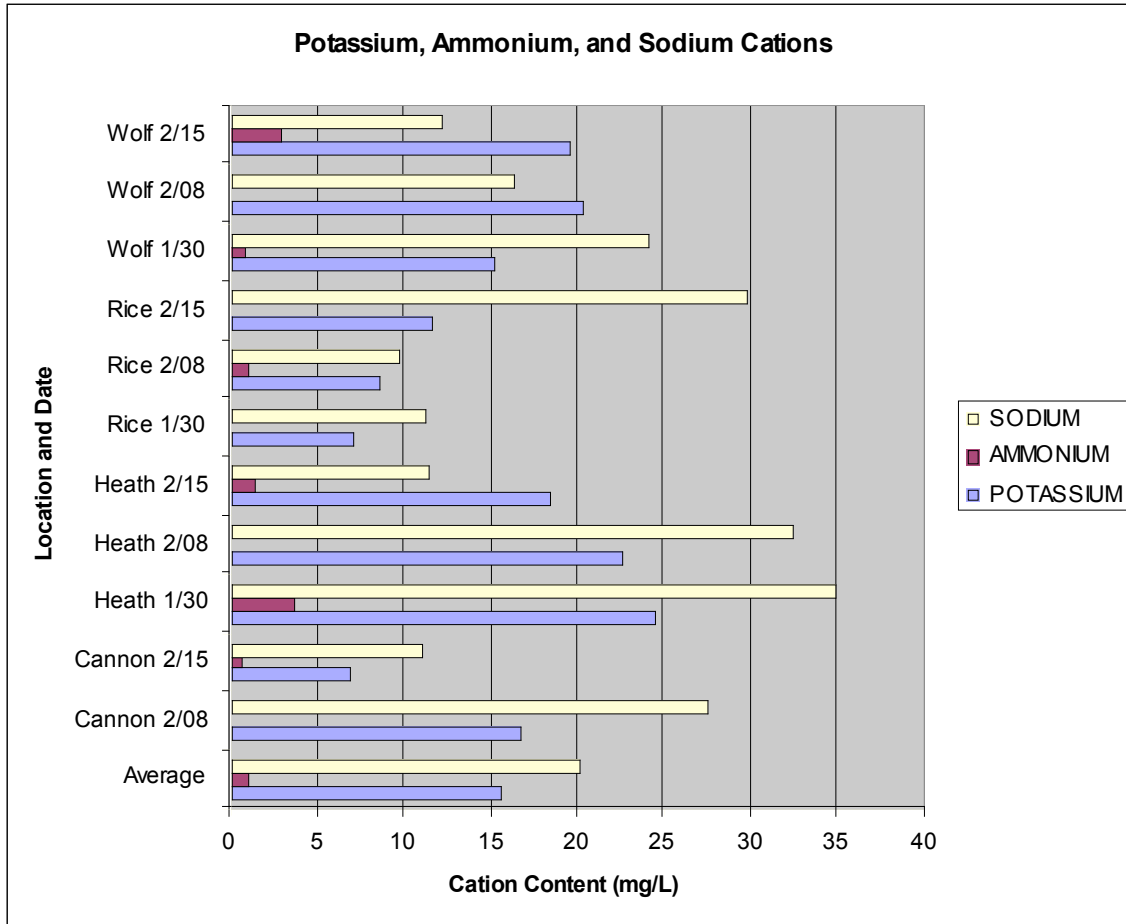


Fig. 4: Potassium, Ammonium, and Sodium cation results by date and location.

Sodium

All samples recorded levels of sodium, ranging from 9.72 mg/L at Rice Creek on February 8, to 34.84 mg/L at Heath Creek on January 30. There is no consistency in fluctuation; that is, no one site has consistently lower or higher values than any other. The average value is 20.03 mg/L. See Figure 4; for complete results, see Appendix B.

DISCUSSION

Conductivity

Conductivity is a measurement of how well water conducts electricity, which is affected by salinity and the amount of material suspended in the water. Dissolved solids such as many of the cations we tested increase conductivity, so the conductivity can be used to estimate relative ion concentration. Furthermore, conductivity is affected by temperature and so will be higher with warmer temperatures. Unsurprisingly, changing conductivity levels will indicate a change in rivers' quality; while rivers' conductivity tends to increase farther downstream, a marked increase in conductivity is likely to indicate the introduction of pollutants.

Looking exclusively at our data, some of the variations have potentially simple explanations. It seems very logical that the conductivity reading at our site in Faribault would be high because our sample location was directly downstream of the drainage for the Faribault Dairy Company. It is heartening that then the conductivity has dropped as we get further downstream to the next Cannon River sample location, indication that the river stabilizes itself and is not overwhelmed by pollutants. The low levels at Wolf Creek might be indicative of a very healthy or unpolluted creek. It is interesting to add here that there was minimal precipitation during the time of our study, and the weather was very mild for all of January and the beginning of February before it dropped significantly mid-February; precipitation can have a marked effect on conductivity. This relative moderation in precipitation and temperature would explain why, for the most part, there are no drastic variations within sample locations.

To compare our findings to the previous studies, it appears as though all conductivity readings are lower on the whole. This would make sense, as the other studies were conducted either at the beginning or end of a farming season and the Cannon River runs through a predominantly agricultural region. Furthermore, the significantly lower temperatures would lead to lower conductivity readings as well. The EPA defines 50 to 1500 μs as an acceptable range for conductivity levels in rivers and streams. Across the board, our findings place the Cannon and its tributaries well within this range, and, certainly as far as can be indicated by the conductivity, the river appears to be cleansing itself during the agricultural off-season.

Temperature

Our temperatures ranged from zero to 3.5°C, which is completely unsurprising due to the timing of our study. In the Fall 2004 Carleton studies, temperatures ranged from 6.7° to 14.1° in Rice Creek, and 8.8° to 16.1° in Wolf Creek. However, streams will be significantly warmer in the fall months than in January and February. The temperature has an affect on the conductivity, which is noted in our conductivity section. The timing of our project placed us in a decidedly wintery, but relatively mild, few weeks.

Ammonium

For the ammonium cation, we found amounts ranging from as low as 0 mg/L to as high as 3.62 mg/L. All of the locations tested for ammonium came up with 0 mg/L at least once. On the 30th of January Heath Creek tested at 3.63 mg/L, the next highest concentration coming from Wolf Creek on the 15h of February, with 2.96 mg/L.

Ammonium in large quantities can be toxic to fish and other marine life and is often caused by sewage leaking into river bodies, so the low occurrence of ammonium in the Cannon River and its affiliate bodies is a good sign. Research done in spring of 2004 found that ammonium existed in quantities ranging from 0.27 mg/L to 2.06 mg/L, but was only evident in 2 of 19 samples whereas we discovered it in 6 of 11 samples. That being said, the amount of ammonium present is not significant in either study.

Calcium

The only calcium levels we have to compare with are the findings from the advanced Carleton College group study from March 2004. They found, in the Prarie-Du-Chien aquifer, calcium levels to be amongst the highest, ranging from 39 to 110 mg/L. This is consistent with other studies of water in Rice County, and our findings land snugly within this range. Calcium in groundwater is not regulated by the EPA as no major health concerns are associated with high or low amounts in water. It is not surprising that calcium levels are high in this region because the Cannon River Valley has many high-calcium soils and minerals, such as the dolomites. Our calcium levels are not particularly revolutionary, and speak to the continued health of these waters.

Magnesium

Our magnesium results present a range from 40.96 mg/L to 66.25 mg/L, which is very consistent with the findings of the Carleton group from March 2004. They had a range, full of variety, from 28.94 to 63.14 mg/L. Ours appear, then, to be slightly less varied but consistent with their findings. It is likely that because our samples were taken in the

winter the water quality is more stabilized. Magnesium is a common mineral in the Cannon River Valley, like calcium, because both minerals are found in dolomite, which is a significant part of the Cannon River rockbed.

Potassium

In testing for potassium within our locations of Cannon River, Heath Creek, Rice Creek, and Wolf Creek we found that potassium was present within every sample in fact had a fair amount within each sample. For instance when looking at the percentage at which potassium was present within each sample testing in comparison to other cations it has consistently stayed close to the same amount and has managed to stay at a moderate amount within each water sample, as seen in the chart below. Seeing as our test groups were taking samples during the winter season as opposed to fall or spring, the results differ in comparison. Our samples had a consistent and moderate amount of potassium within every location, ranging from 7 mg/L at the lowest to 24 mg/L at the highest. In previous work done in Spring 2004 within Rice County, potassium levels were inconsistent and for the most part relatively low. Ranging from 0.97 to 7.50 mg/L with one 89.62 mg/L, the range varies in comparison to our sample testing which had an average of 15.57 mg/L.

The same previous data discussed that the same wells had high levels of nitrates thus indicating a presence of fertilizer. In looking at the results from previous work the presence of fertilizer did not present a high risk from high potassium levels. Therefore, in looking at the seasonal affects of nitrates and potassium, the presence of fertilizer was not as prevalent within our testing samples this winter. Since much of the locations for the

testing sites were located near farming areas, presence of nitrates and fertilizer during farming seasons in the fall and spring makes sense. Given that our testing was done during the winter season, it makes sense that our potassium levels were lower. One of our testing locations, Heath Creek, was located near the Bonita Rae farm, and did not have as much of an indication of fertilizer, but did of potassium, which can be attributed to the season.

Sodium

Analysis of the sodium cation revealed sodium presence starting at 9.72 mg/L, found in Rice Creek on the 8th of February, and reaching a high point of 34.84 mg/L at Heath Creek on the 30th of January. Sodium was present in all samples. This is consistent with data collected in March of 2004 which ranged from 5.42 mg/L to 45.31 mg/L. The recommended amount of sodium for domestic water is 20 mg/L, which is roughly to what our findings average out. It is also worth noting that this is unfiltered water that is not intended for human consumption, so there is no cause for alarm with regards to sodium presence.

CONCLUSION

All of our results point to the continued health of the Cannon River and its tributaries. All of our cation analysis finds them within acceptable ranges and are consistent if not lower than the findings of previous Carleton groups. Perhaps most indicative of the water's health during the winter are the conductivity levels, which were lower across the board than spring and fall conductivity readings. While the conductivity levels would naturally be lower during the winter season, they also speak to the lower levels of suspended material in the water, thus indicating a decreased amount of pollutants. Our cation analysis is consistent with this finding. Due to limitations imposed by cold weather, we only collected three samples from each site and all were representative of mild winter conditions. Our recommendation for future study is to continue to monitor these sites in addition to others while increasing the scope and frequency of the monitoring in order to provide a more complete picture of the Cannon River's health.

ACKNOWLEDGMENTS

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APPENDICES

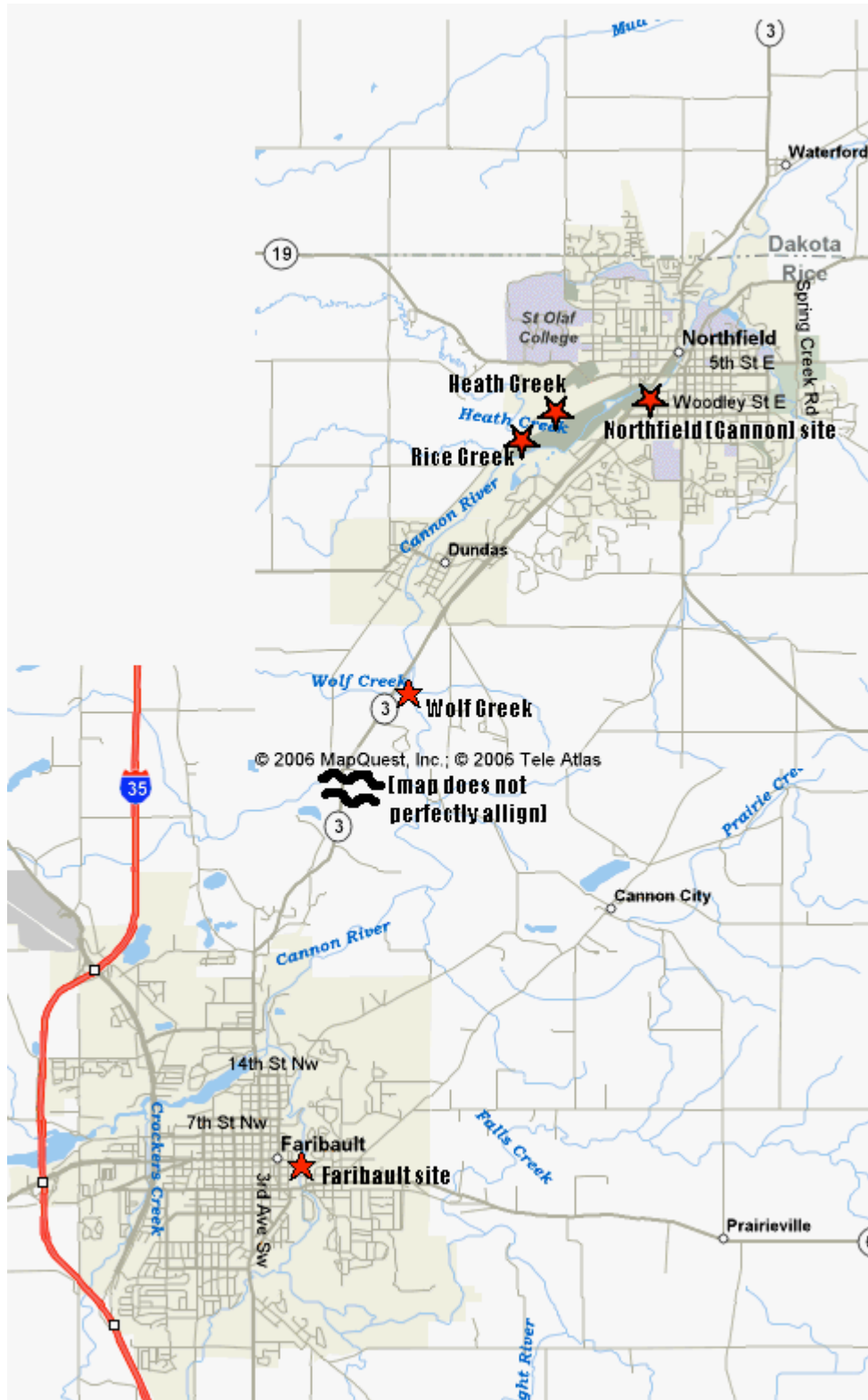
Appendix A: Temperature and Conductivity Readings

Date and Location	Temperature (Celsius)	Conductivity (microsiemens)
Cannon 1/30	1.8	389
Cannon 2/08	0.5	232.5
Cannon 2/15	0.4	382.2
Heath 1/30	1.0	339.4
Heath 2/08	0.0	348
Heath 2/15	0.0	350.9
Rice 1/30	3.5	388.8
Rice 2/08	1.0	340
Rice 2/15	1.2	388.2
Wolf 1/30	2.8	305.1
Wolf 2/08	0.2	255.1
Wolf 2/15	0.2	267.7
Faribault 2/08	2.4	474
Faribault 2/15	0.5	421.1

Appendix B: Cation Readings

Date and Location	Ammonium (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)
Cannon 2/08	0.0	73.54	58.99	16.70	27.40
Cannon 2/15	0.65	78.97	62.04	6.89	11.04
Heath 1/30	3.62	64.37	52.33	24.45	34.84
Heath 2/08	0.0	67.47	54.18	22.59	32.46
Heath 2/15	1.29	53.55	43.75	18.44	11.44
Rice 1/30	0.0	77.23	62.63	7.00	11.18
Rice 2/08	1.05	72.05	55.36	8.63	09.72
Rice 2/15	0.0	86.46	66.25	11.56	29.82
Wolf 1/30	0.85	75.12	59.18	15.17	24.15
Wolf 2/08	0	53.58	41.71	20.35	16.23
Wolf 2/15	2.96	51.17	40.96	19.52	12.11

Appendix C: Map of Testing Locations



Appendix D: Tables of Previous Research

Table 1.1: First Chart of Previous Research, from Carleton College (CC) students

	Results Category	CC March '04 Praire-du-Chien	Outside Resources Used by CC 3/04	CC Fall '05 CRWP
A N I O N S	Bromide	Not found	n/a	Not found
	Phosphate	Not found	n/a	Discharge rate: 0 (both sites)
	Sulfate	Always present, range from 0.11 to 62.93 mg/L	(data from Rice County ion chromatograph (IC) tests) range of 8.72 to 62.93 mg/L; MN PCA determined no aquifers have elevated concentrations (500 mg/L is max. con.)	Site 1: 75.76 Site 2: 475.26
	Chloride	Always present, range from 0.08 to 72.54 mg/L	(data from Rice County IC tests) range from 0.08 to 72.54 mg/L	Site 1: 4.75 Site 2: 46.36
	Fluoride	Always present, range from 0.14 to 0.32 mg/L	MN PCA determined no aquifers have elevated concentrations (4 mg/L is max. con.)	Site 1: 0.10 Site 2: 0.51
	Nitrate-N	14 /19 samples, range from 0.0 to 13.52 mg/L	MN Dept. of Health puts limit at 10 mg/L; previous studies (1999) had not indicated these high levels; Jordan aquifer has highest levels of Nitrite in MN (GWMAP), most of Rice County in “high risk” zone	Site 1: 0.07 Site 2: 0.77
	Nitrite-N	3/19 samples, range from 0.14 to 0.83 mg/L	Small amounts attributed to microprobe origin	Not found
C A T I O N S	Ammonium	2/19 samples, range from 0.27 to 2.06 mg/L	Concern about ammonium levels when in correlation with nitrates; no large ammonium presence nor ammonium in wells with nitrates	Not found

	Lithium	“Extremely low,” max. con. of 0.65 mg/L	Often not present, no further investigation	Not found
	Sodium	Always present, range from 5.42 to 45.31 mg/L, most under 25 mg/L	No cause for alarm	Site 1: 6.5 Site 2: no data
	Potassium	“Relatively low,” range from 0.97 to 7.50 mg/L with one 89.62 mg/L	Outlier occurred at same well with highest nitrate value, indicating fertilizer; no high risk from high K levels.	Site 1: 3.9 Site 2: no data
	Magnesium	“Varied” from 28.94 to 63.14 mg/L	Both Mg and Ca abundant in minerals and soils, esp. dolomites	Site 1: 54.6 Site 2: no data
	Calcium	“Higher”, range from 39.08 to 109.03 mg/L		Not reported
STABLE ISOTOPES	$\delta^{18}\text{O}$	Ranges from -8.67	Both consistent with regional meteoric discharge; consistent with data from 1964 in range for meteoric waters in this region	n/a
	δD	Ranges from -54.00 to -75.00		n/a

Table 1.2: Second Chart of Previous Research, from Fall '04 CC Data

	Results Category	Heath Creek	Rice Creek	Wolf Creek
OTHER TESTS	Conductivity	Around 400 to 500 μs	Generally around 450 to 550 μs	Generally around 250 to 350 μs
	Dissolved O	Not reported	Ranged from 4.43 – 15.55 mg/L	Averaged 8 – 11 mg/L
	Salinity	Not reported	Inconclusive data; was 0.3 ppt in spring 03	Not reported
	Temperature	Not reported	Ranged from 6.7° to 14.1° C	Ranged from 8.8° to 16.1° C
A	Bromide	Not found (0.0)	Not reported	Not reported
N	Phosphate	Not found (0.0)	Not reported	Not reported

I O N S	Sulfate	Always present, range from 0.16 to 0.22 mg/L	Ranged from 11.87 to 24.65 mg/L	Averages ranged from 21.32 to 28.86 mg/L
	Chloride	Always present, range from 0.16 to 0.26 mg/L	Ranged from 20.08 to 29.04 mg/L	Averages ranged from 10.84 to 12.28 mg/L
	Fluoride	Always present, range from 0.10 to 0.12 mg/L	Not reported	Not reported
	Nitrate-N	Undetectable in first 6 km, range from 0.0 to 0.80 mg/L	Ranged from 8.82 to 20.14 mg/L	Averages ranged from 1.90 to 3.61 mg/L
	Nitrite-N	Trace amounts detectable in lower half, range near 0.16 mg/L	Not reported	Not reported
CA TIO N	Calcium	Not reported	Not reported	Ranged from 13 to 23 mg/L

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The following websites are information about the Cannon River as supplied by either the United States Geological Survey (USGS) or the Minnesota Geological Survey (MGS).

- a. http://waterdata.usgs.gov/usa/nwis/uv?site_no=05355200
- b. http://waterdata.usgs.gov/nwis/current?huc_cd=07040002&index_pmcode_00065=3&index_pmcode_00060=4&index_pmcode_00062=5&index_pmcode_72020=6&sort_key=site_no&group_key=county_cd&sitefile_output_format=html_table
- c. <http://waterdata.usgs.gov/mn/nwis/current/?type=quality>
- d. http://nwis.waterdata.usgs.gov/mn/nwis/qwdata?qw_count_nu=1&begin_date=&end_date=&format=html_table&site_no=05352010&agency_cd=USGS
- e. http://nwis.waterdata.usgs.gov/mn/nwis/qwdata?qw_count_nu=1&begin_date=&end_date=&format=html_table&site_no=05355090&agency_cd=USGS