

AN ABSTRACT OF THE THESIS OF

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Title: Changes in the surface water of the Marais de Cygnes River, 1964 - 1998

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Acid precipitation has been moving westward in the past few decades. One way of determining the extent of acid precipitation is to evaluate the acidification of surface water. This study compared current with past ratios of alkalinity (HCO_3^-) to hardness (Ca^{+2} & Mg^{+2}) as a measure of the acidification of the Marais de Cygnes River in east-central Kansas. At low to moderate discharge, the ratio showed no significant change, but this study found a decrease at high discharge compared with the data from the 1960s. The ratio was lowest in March, June and November, and highest in August. A site immediately downstream from Melvern Dam had consistently lower ratios than a site located further downstream in the city of Ottawa.

CHANGES IN THE SURFACE WATER OF
THE MARAIS DE CYGNES RIVER, 1964 TO 1998

A Thesis

Presented to

The Division of Physical Sciences

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

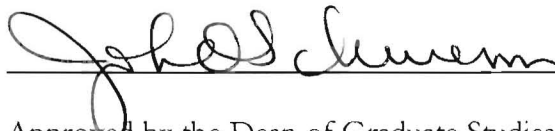
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Thesis
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Approved by the Division Chair



Approved by the Dean of Graduate Studies and Research

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GLOSSARY

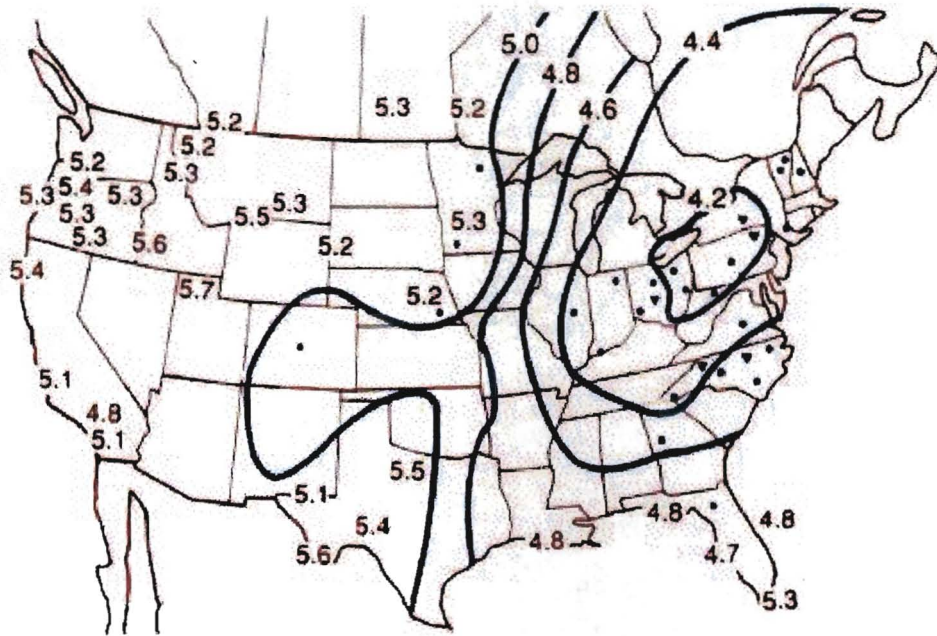
- Anion:** An atom or molecule with a net negative charge.
- Background Interference:** Error caused by ions other than those being tested for. This interference produces a high result but this can be corrected with pretreatment of the sample.
- Cation:** An atom or molecule with a net positive charge.
- Linear Range:** The range on a graph of absorbance versus concentration where the ratio is linear.
- pH:** $\text{pH} = -\log [\text{H}^+]$
- Releasing Agent:** A chemical added to a sample to prevent interference of other compounds in spectroscopy.
- Standard Solution:** A solution of known concentration to which the unknown solution can be compared.
- Titrant:** The solution used to neutralize the unknown during a titration.
- Titration:** An analysis performed by slowly adding a standard solution from a buret to a solution of analyte until the reaction between the two is complete.

Chapter 1

INTRODUCTION

Acid deposition from anthropogenic sources is known to have increased the acidity of surface waters. This is a particular problem in the northeastern United States (American Chemical Society, 1991), and this problem has been spreading westward, although there is no consensus on the rate of expansion or the extent, see figures 1 (Olsen, 1987) & 2 (Nebel, 1990). One way to determine the extent of acid deposition is to examine the effects of acidity of surface water (Schindler, 1988). Testing for surface water acidification is not dependent on precipitation and so sampling can be done at scheduled times. The purpose of this study is to determine if there have been changes in the chemistry of the Marais de Cygnes River in the past three decades that can possibly be attributed to acid deposition.

The technique used in this study examines the ratio of alkalinity as measured by bicarbonate (HCO_3^-) concentration to hardness as measured by calcium and magnesium (Ca^{+2} and Mg^{+2}) concentrations to determine if the river has undergone acidification. If acidification is occurring, Ca^{+2} and Mg^{+2} concentrations will increase and bicarbonate concentrations will decrease (Schindler, 1988) as the acid neutralizes bicarbonate formed during weathering of carbonate minerals. This would be reflected in a lowering of the alkalinity to hardness (A/H) ratio. This methodology is especially useful in areas such as Kansas because pH changes are not a reliable measurement of acidification if the water



Acidity of North American Precipitation, 1985 (measured in pH units)

Figure 1: Extent of Acidification 1985 (Olsen, 1987)

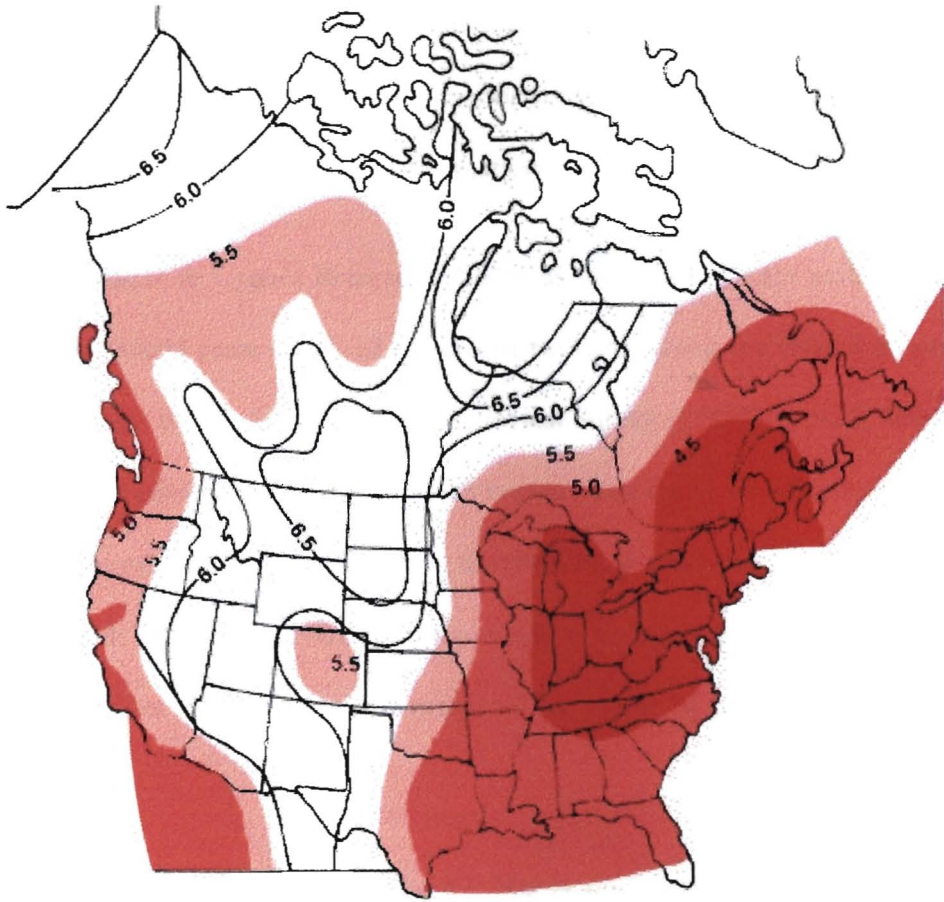


Figure 2: Extent of Acidification 1990 (Nebel, 1990)

body has not lost a significant portion of its buffering capacity (Schofield, 1982). Kansas, having mostly calcareous bedrock, either limestone or calcareous shale (Moore, 1951), is an excellent example of the area in which this method works best. This use of a ratio is also preferred because it avoids day to day fluctuations in pH measurements.

The Marais de Cygnes River was chosen as the study area for several reasons. First, this river has several years worth of data from two sites along the river that were collected over 30 years ago by the United States Geological Survey (USGS) (USGS, 1964, 65, 66, 67, 68). These data provide a baseline to which current data could be compared. Second, there have been two major changes concerning the river since 1968; the building of Melvern Dam and city growth in Ottawa. Third, it was possible to collect samples from three sites (figure 3) along this river allowing an assessment of the acidity along different segments of the river.

Three sites were sampled along the Marais de Cygnes River. Site 1 and Site 2, for which previous data were available, are down river of Melvern Dam and Site 3 is upstream of the dam. These three sites were used for two comparisons. The data from Site 1 and Site 2 were compared to the data from 1964 - 1968 to determine if there had been changes in river chemistry over time. Site 3 was used as a proxy for Sites 1 & 2, 30 years ago and compared to Site 1 & 2 data from the 1960s to determine what effect the construction of Melvern Dam and urban development in Ottawa may or may not have had on the river chemistry. Site 3 was far enough upriver from both Ottawa and the dam at Melvern Lake that effects of the dam and Ottawa on the river chemistry would not be felt at this site.

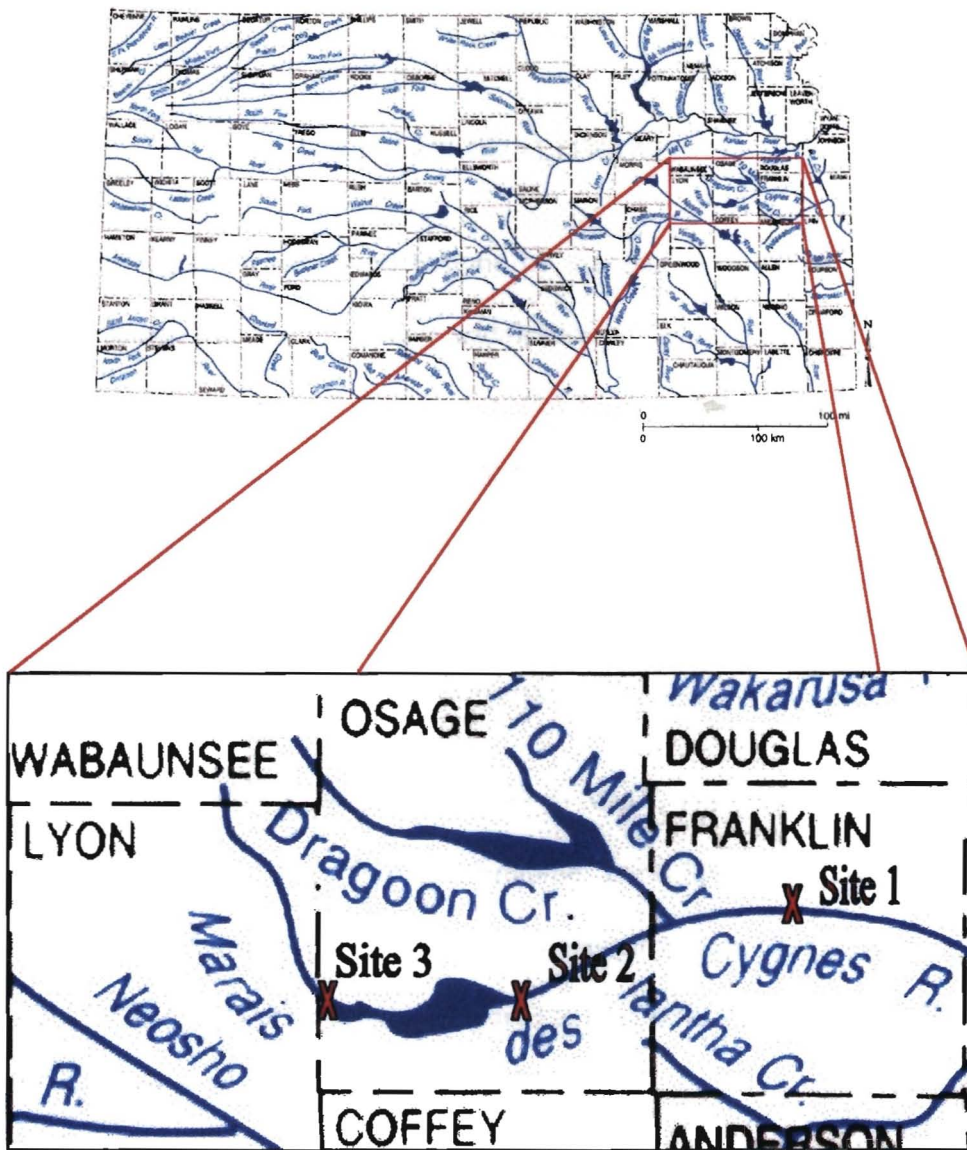


Figure 3: Map of Kansas Rivers Showing All Sites on the Marais de Cygnes River

BACKGROUND LITERATURE

Monitoring changing concentrations of the acid neutralizing capacity (ANC) of surface water is one way to determine if acidification of the surface water is taking place. In the Blue Ridge and Valley and Ridge provinces of Virginia, over a period of 13 days, Webb et al. (1989) gathered water samples from 344 streams. The base cations (H^+ , Ca^{+2} , Mg^{+2} , Na^{+2} and K^+) as well as the strong acid anions (Cl^- , NO_3^- , SO_4^{-2} and HCO_3^-) were measured for each sample collected. These ions were compared to previous data to determine if acidification of the chosen streams had occurred.

This 13 day period, from April 24, 1987 to May 7, 1987, was chosen because earlier studies indicated that "winter and springtime concentrations provide the closest approximation of volume-weighted annual mean concentrations" (Webb et al., 1989). Due to this, and the fact that data was only compared to data from March 1982, an entire year of sampling was deemed unnecessary.

The regions in the study by Webb et al. (1989) have a geological character quite unlike Kansas. The bedrock of the Valley and Ridge province is primarily granites, granulites and metabasalts faulted into steep sided mountains. Carbonate rock is typically only found in the valleys and topographically low areas of this region. The samples in the Webb et al. study were taken only from streams where the agricultural, industrial and

residential influences were minimal. A few additional streams that drained carbonate terrain or were difficult to access were also excluded.

The water samples were collected after a period of above average precipitation in the area, but Webb et al. (1989) determined this had little to no effect on the results based on their comparison to previous data from March 1982 and water samples collected weekly from Shenandoah National Park nearby.

The results of the Webb et al. (1989) study showed that a startling majority of the streams sampled (93%) had alkalinity concentrations under 200 $\mu\text{eq/L}$, the commonly accepted limit between normal and acid sensitive waters. They also found that 49% of the streams had alkalinity $< 50 \mu\text{eq/L}$ denoting extremely acid sensitive water and 10% of the streams had alkalinity $\leq 0 \mu\text{eq/L}$ indicating acid waters.

Webb et al. (1989) concluded that streams in the Valley and Ridge province were acidifying more rapidly than in the Blue Ridge province. They attributed this to the greater abundance of carbonate sedimentary rocks, which raised the carbonate concentrations, in the Blue Ridge province. Webb et al. (1989) also found that sulfate was the major anion found in the streams suggesting that sulfate deposition was a major cause of the acidification in this area.

Baker et al. (1991) did a similar study of lakes and streams across the United States. They found 1,180 acid lakes and 4,670 acid streams across the United States that were related to acid deposition. All of these water bodies were part of the National Surface

Water Survey (NSWS) administered by the Environmental Protection Agency (EPA). The water bodies were separated into three categories:

1. Organic dominated surface waters, where organic anions exceeded sulfate (SO_4^{-2}) and nitrate (NO_3^-) regularly.
2. Waters dominated by watershed sources of sulfate, where sulfate (SO_4^{-2}) concentrations were greater than twice as high as predicted.
3. Deposition dominated waters, where sulfate and nitrate from acid deposition dominated.

Baker et al. (1991) tested for alkalinity, SO_4^{-2} and NO_3^- to determine areas of high surface water acidification. They found six major regions of acidity across the country: eastern Upper Midwest, southwest Adirondacks, New England, forested Mid-Atlantic Highlands, Mid-Atlantic Coastal Plain and north Florida Highlands. Other areas of high acidification were found in the Rocky Mountains as well as western Arkansas and eastern Oklahoma.

In these areas, an extraordinary 68% of the acidic water bodies were found to be deposition dominated. Of the acidic water bodies, 75% of the lakes and 47% of the streams were the result of acid deposition while only 25% of all the sampled water was found to be dominated by organic acids.

Many of the lakes and streams found in these regions of acidity ran through crystalline bedrock and low alkalinity soils. In the Midwest, most of the acidity in the surface water corresponded with forested watersheds leading Baker et al. (1991) to conclude

the causes of the acidification in these areas was from atmospheric deposition, forest re-growth, or in the coastal areas, retention of sea-salt.

In 1997, Indra Bhangu and Paul H. Whitfield looked at changes in water quality of the Skeena River in Usk, British Columbia. Bhangu and Whitfield (1997) measured 21 ions in the river including pH, bicarbonate, Ca^{+2} and Mg^{+2} concentrations. Each of the ions was plotted against discharge in a hysteresis diagram (log-log) to determine if there was a lag time between changes in discharge and changes in water quality.

Bhangu and Whitfield (1997) found strong seasonal associations for many of the ions. The pH of the samples showed no seasonal variation but they found a negative relationship to discharge. Bicarbonate also exhibited this negative relationship to discharge. Discharge was at its greatest in May and June with another high in October, corresponding to times of snow-melt and high precipitation.

Likens, Driscoll and Buso (1996) tested stream-waters in New Hampshire for acidification. They found that not only has the pH and ANC decreased since 1940, levels of Ca^{+2} and Mg^{+2} in the soil have also decreased while Ca^{+2} and Mg^{+2} concentrations in the water have increased. The study by Likens et al. (1996) showed that ion concentrations in both soil and water buffering are not rebounding as acid input decreases.

Schindler (1988) studied the effects of acid rain of freshwater ecosystems. He used a different technique to determine acid sensitivity rather than simply measuring the amount of bicarbonate (ANC) in the water. He measured the alkalinity of the water, as determined by bicarbonate (HCO_3^-) concentration and the hardness of the water, measured by Ca^{+2} and

Mg^{+2} concentrations. He used these measurements to determine a ratio of alkalinity to hardness (A/H). If the ratio A/H falls below 0.6 the water body can be classified as acid sensitive. Using this technique, Schindler (1988) concluded that lakes of the northeastern United States were acidifying at a slower rate than had been suggested by previous data.

This study uses Schindler's method of acidification determination in surface waters. This method was chosen because it factors in all the possible ways the water can be affected by acids. Many of the other methods described above are used when the water is known to be acidifying and the reason for acidification is already suspected.

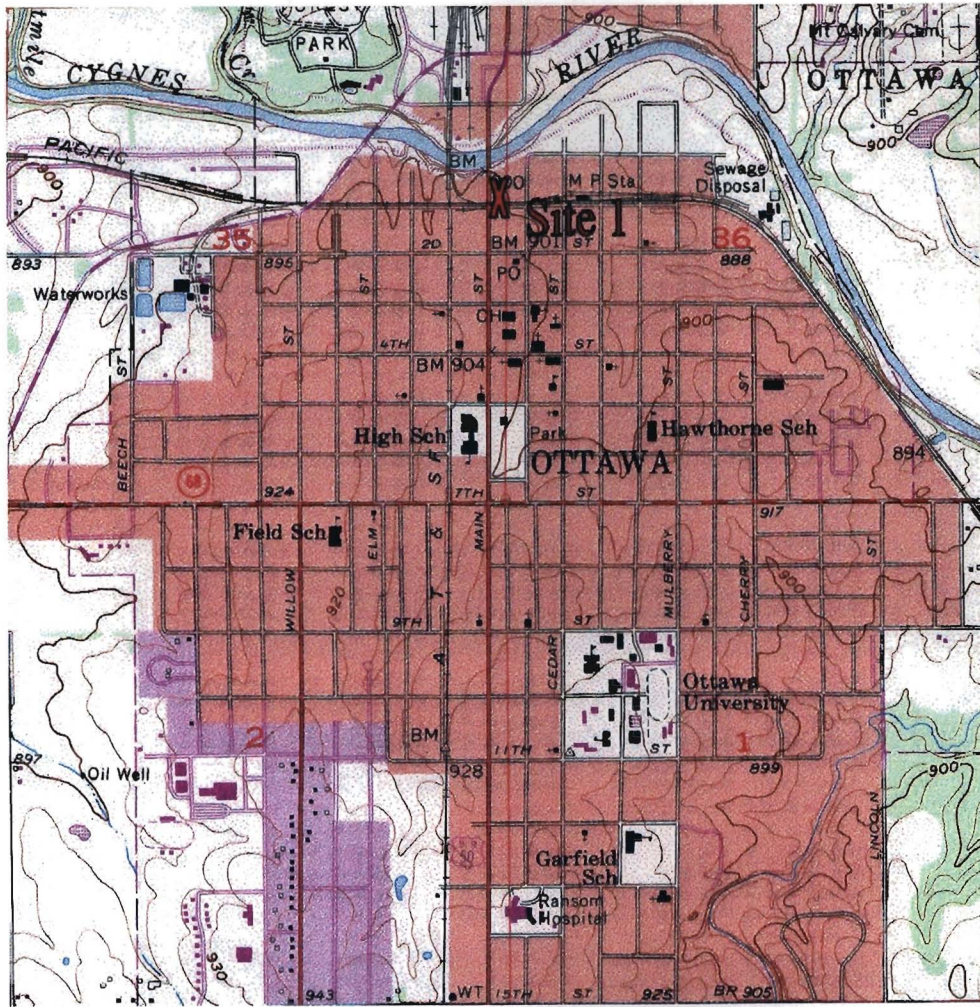
Chapter 3

SAMPLING SITES

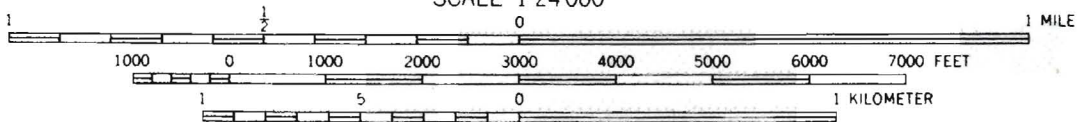
Three sites on the Marais de Cygnes River were chosen for the sample area (see figure 3). Samples from Site 1 were taken adjacent to the bridge of highway 59 in Ottawa (see figure 4, plates 1 & 2). Site 2 samples were taken adjacent to the bridge of highway 31, synonymous to Highway 75 from the 1960s, just below Melvern Lake (see figure 5, plates 3 & 4). Site 3 samples were taken adjacent to the bridge of highway 170 (see figure 6, plates 5 & 6). It was important to sample both above (Site 3) and below (Site 1 & Site 2) the lake so any effects Melvern Dam had on the river would be noted.

Table 1: Locations of the three sample sites for this study

	¼	¼	¼	Section	Township	Range	Quadrangle	GPS Coordinates (UTM zone 15) ±5m
Site 1	NE	SE	NE	35	16 S	19 E	Ottawa South, KS	0302495 m E 4276860 m N
Site 2	NE	SE	NE	1	18 S	15 E	Lyndon, KS	0265297 m E 4266624 m N
Site 3	NW	NE	NE	1	17 S	13 E	Reading, KS	0245220 m E 4267641 m N



SCALE 1:24 000



CONTOUR INTERVAL 10 FEET
 NATIONAL GEODETIC VERTICAL DATUM OF 1929

Figure 4: Map of Site 1, Ottawa South Quadrangle



Plate 1: View of the Marais de Cygnes river at Site 1 looking west from the south bank. Note the scale bar to the left. Scale is in 10 cm increments.



Plate 2: View of the Marais de Cygnes river at Site 1 looking east from the south bank. Note the scale bar to the right. Scale is in 10 cm increments.

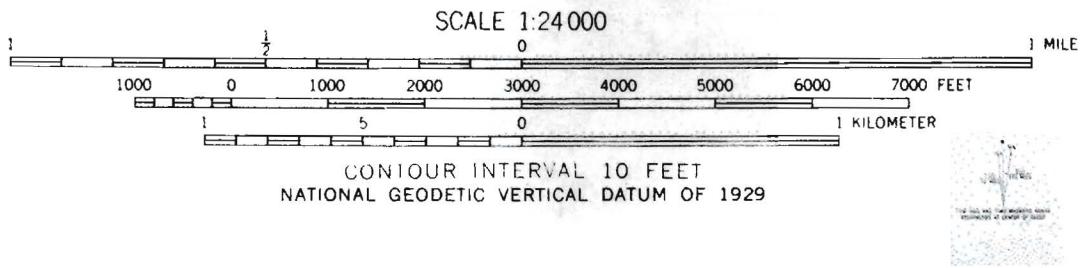
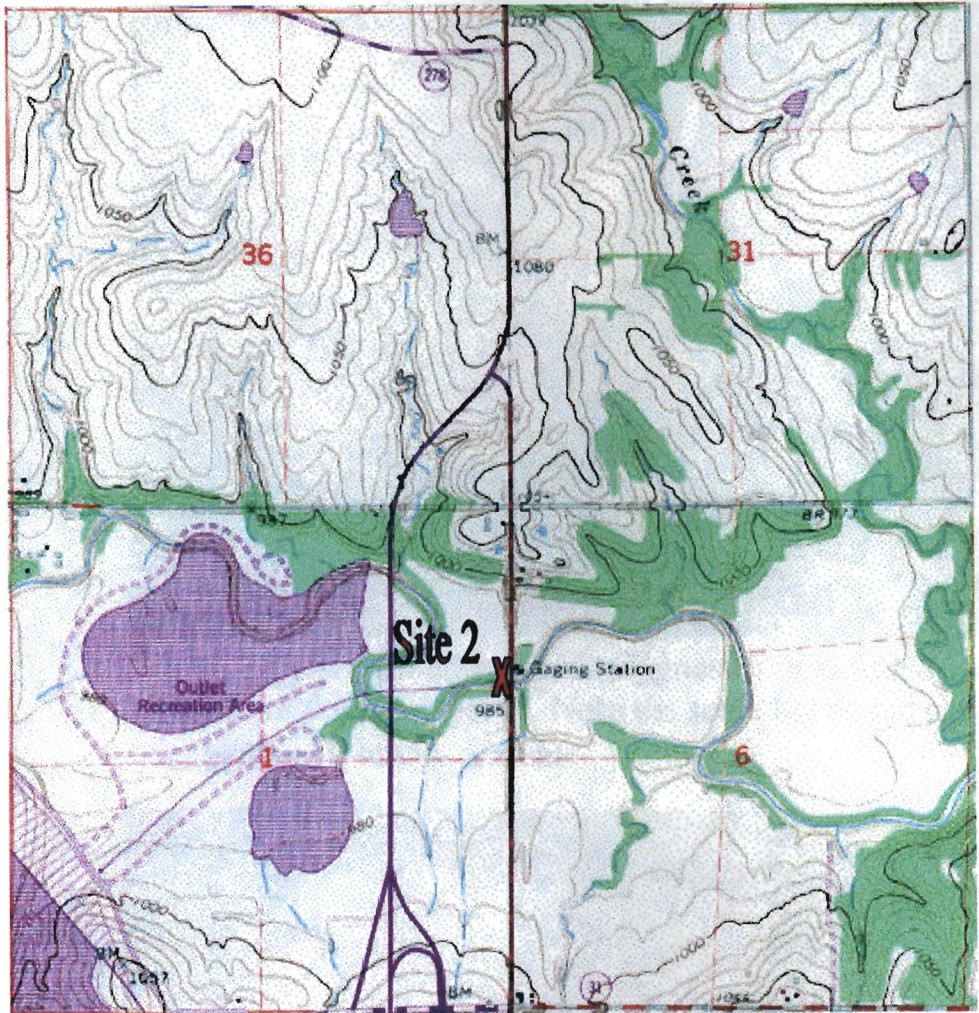


Figure 5: Map of Site 2, Lyndon Quadrangle



Plate 3: View of the Marais de Cygnes river at Site 2 looking west from the north bank. Note the scale bar in the center. Scale is in 10 cm increments.

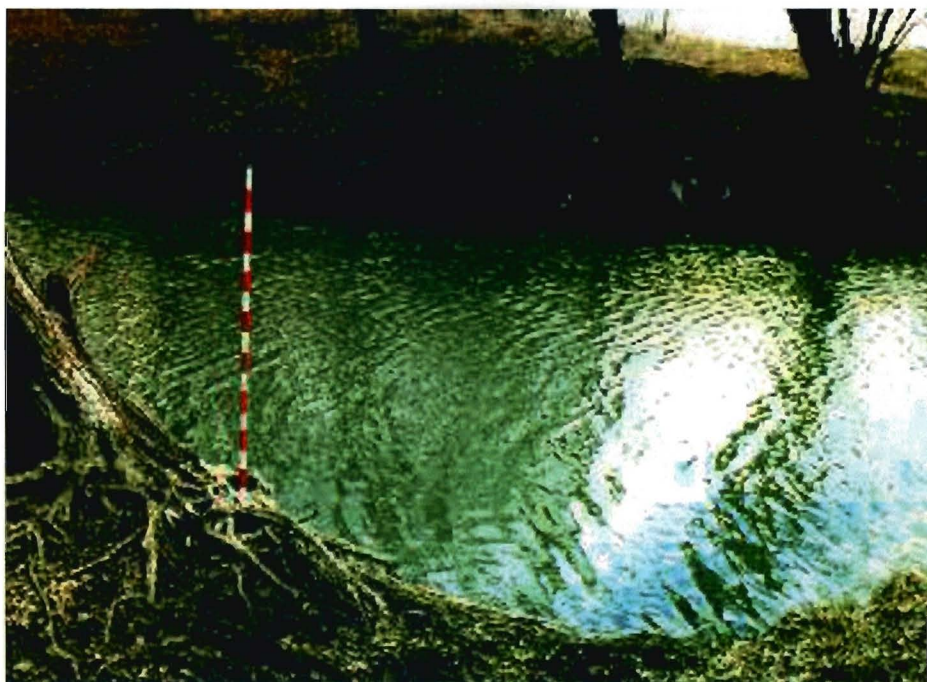
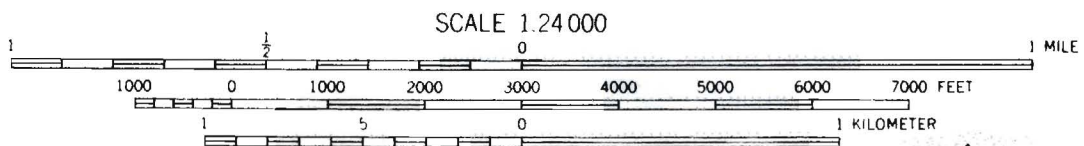
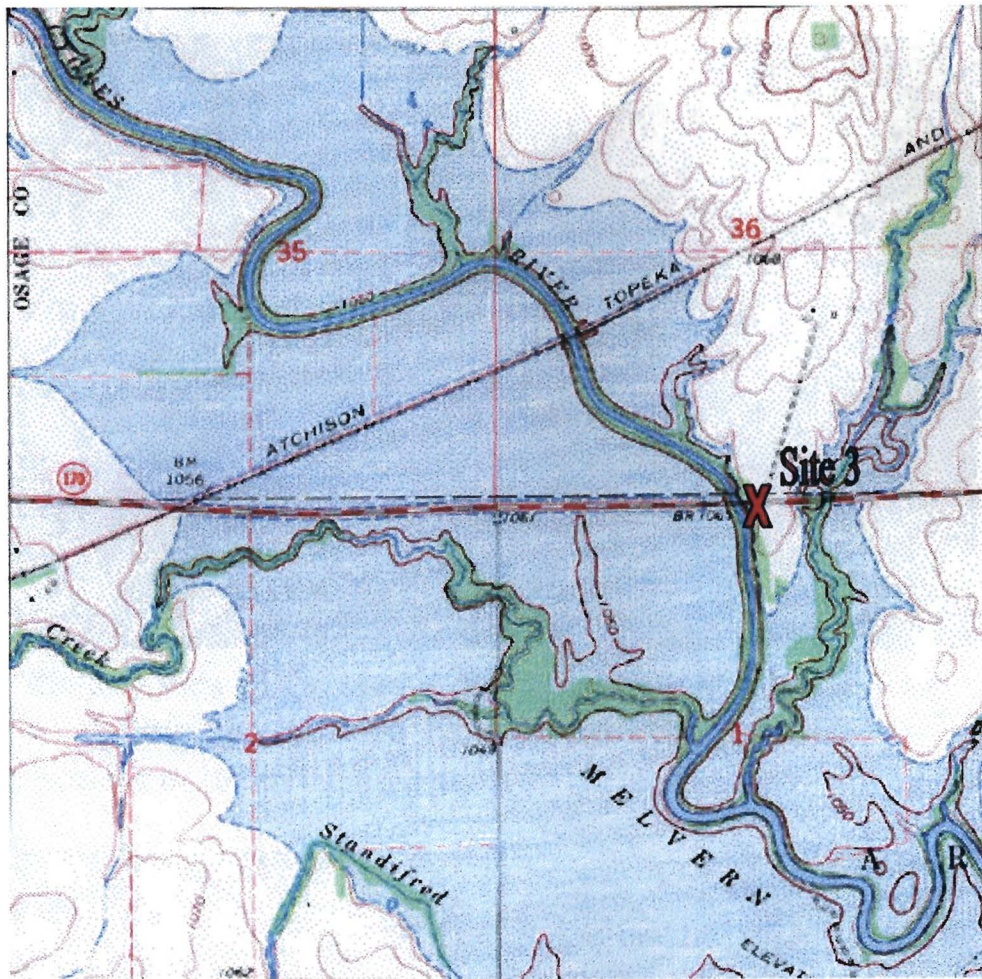


Plate 4: View of the Marais de Cygnes river at Site 2 looking south from the north bank. Note the scale bar to the left. Scale is in 10 cm increments.



CONTOUR INTERVAL 10 FEET
 NATIONAL GEODETIC VERTICAL DATUM OF 1929



Figure 6: Map of Site 3, Reading Quadrangle



Plate 5: View of the Marais de Cygnes river at Site 3 looking south from the east bank. Note the scale bar to the left. Scale is in 10 cm increments.



Plate 6: View of the Marais de Cygnes river at Site 3 looking north from the east bank. Note the scale bar to the right. Scale is in 10 cm increments.

Sites 1 and 2 were chosen because they were previous sampling sites of the United States Geological Survey from the 1960s. The choice of sites for this study duplicated as closely as possible the previous sampling sites. The 1968 sampling site in Ottawa was unavailable because a wastewater treatment plant now occupies the earlier sampling location. Sample Site 1 was therefore located approximately one mile upriver to the junction of the Marais de Cygnes River and Highway 59. Site 2 was chosen close to Melvern Dam to allow monitoring of changes in the water resulting from the construction of the dam. Site 3 was not a site of previous testing by the USGS. It was chosen because it lies above Melvern Dam making upstream and downstream comparisons possible.

General visual comparisons of the river channel, flow rate and turbidity were made at each sample site. The depth of the sampling area was measured using a staff marked in 10 cm intervals. The river at Site 1 averaged 0.5 to 1 meter in depth at the point from which samples were taken. This part of the river was about half-way through the city of Ottawa. Ottawa has grown to the north and east since the late 1960s. The urbanization of this area promised to be very interesting because increased urbanization is known to lead to additional pollutants entering the surrounding ecosystem increasing the acidity of the surrounding water (Montgomery, 1997).

Site 2 had the deepest water of the sites with an average water depth of 1.5 to 2.0 meters. The water was quiet and still with a low flow velocity. The change in depth for the river may be attributed to its proximity to Melvern Dam which is less than a kilometer upriver from this sample site. The dam has lowered the discharge in this area causing slower flow rates (USGS, 1965 - 68; Appendix A). Ponding of the water in Melvern Lake

has caused the suspended sediment to fall out of the water column. Presumably, the river has not traveled sufficiently far by the time it reaches this sampling site to increase its sediment load significantly. This segment of the river runs mainly through lands reserved for parks and wildlife habitat although there are a few households and farms bordering the river.

Site 3 had the highest apparent turbidity of the three sites and also appeared visually to have the highest sediment load. This site was more similar to Site 1 than Site 2. The river at Site 3 runs through marsh and farmland. The nearest town was Reading which lay 1.6 kilometers upstream to the west on highway 170.

The bedrock at all three sites is overlain on the floodplain by the Verdigris and Osage soils which are deep, nearly level, well to poorly drained soils that have silty or clayey subsoils. Both of these soils are neutral to medium acid in composition. All three sites along the Marais de Cygnes are on Quaternary alluvial deposits although the underlying bedrock is different at each site.

Table 2: Typical bedrock and soils of all sampling sites

Site	Group	Primary Rocks found	Soil
1	Douglas	Limestone and shale with some sandstone	Verdigris-Osage
2	Shawnee	Limestone and shale	Verdigris-Osage
3	Wabunsee	Limestone and shale	Verdigris-Osage

Chapter 4

METHODS

Field Methodology

Samples from all three sites were collected using a 1.82 meter pole and a 1 liter polyethylene bottle. The bottle was filled with water from approximately 0.5 meter below the water surface at Sites 1 and 3 and approximately 1 meter below the surface at Site 2. Sampling below the surface of the river kept floating debris out of the sampling bottle.

Sample procedures used by the USGS are described in *Methods for Collection and Analysis of Water Samples* (Rainwater and Thatcher, 1960) which recommends the use of hard rubber, polyethylene or other plastic container for collection as glass is susceptible to breaking. Rainwater and Thatcher (1960) suggest that when sampling from a bridge, that one use a sampler suspension apparatus. Although this is the preferred method, wading and sampling closer to the edge via a pole, the method used in this study, is also an accepted method.

At each site, air and water temperatures were measured to the nearest 0.5 degree Celsius using an alcohol thermometer. Temperature measurements are necessary to accurately correct the sample pH readings because as the temperature of a solution changes

the pH value also changes. This solution pH change can be modeled using the Nernst equation as found in Westcott, 1978:

$$E_{obs} = E^{\circ} + S \log (a_{H^+})$$

Where E_{obs} = the observed electrical potential, E° = the stable fixed potentials including reference internal potential and S = the slope. The above equation can be rewritten by substituting $-pH$ for the $\log (a_{H^+})$ giving the next equation:

$$E_{obs} = E^{\circ} - S pH$$

The slope has been found by experimentation to be $0.198T_k$ giving the final equation of:

$$E_{obs} = E^{\circ} - 0.198T_k pH$$

where T_k = temperature in Kelvin, showing that pH will change as the temperature changes (Westcott, 1978). Therefore it is necessary to calibrate the pH meter in buffer solutions that are the same temperature as the unknown solution.

The pH of the water was measured at each site immediately after collection. While measuring the air and water temperatures, the pH standard solutions (pH 4 and pH 7) were placed in the river to bring them to the same temperature as the water. The pH of these

two standard solutions was measured before testing the pH of the water using a Checker glass electrode pH meter. The pH meter was first rinsed with distilled water and then with the next sample between each reading to prevent contamination.

The observed pH values of the water samples were later corrected using a spreadsheet in Quattro Pro® and the readings of the standard solutions. This method of correction was better for use in the field than calibrating the pH electrode with the two buffers at each site because the solution temperature could not be controlled in the field as it could in the laboratory and varied slightly over the course of the testing causing the true pH of the standards to vary also. This method of correction also had the added benefit of lowering the risk of contamination between the bottles by carryover of the sample and buffers.

Rainwater and Thatcher (1960) describe the method of pH determination used by the USGS below:

Apparatus and Reagents:

- Beckman pH meter with glass or saturated calomel electrodes
- Buffer solution, pH 7.00 ± 0.02 at 25°C

Procedure:

1. After an appropriate warm-up period, standardize the instrument with the buffer solution at the approximate temperature of the sample.

2. With a minimum of aeration and agitation, measure the pH in accordance with the instrument-manufacturer's instructions.

Laboratory Methods

The samples were analyzed in the laboratory for bicarbonate, Ca^{+2} and Mg^{+2} concentrations. The first analysis of the sampled water was for its bicarbonate (alkalinity) concentration. This analysis was done within 24 hours of sample collection. Bicarbonate concentration was measured using the test described in *Laboratory Manual for Analytical Chemistry* (Schroeder, 1995). This procedure is similar to titration procedures used by others for similar analyses.

Each sample, along with a standard of sodium carbonate (Na_2CO_3) solution, was tested in duplicate. Using a pipet and bulb, 10 ml of 0.0250 M Na_2CO_3 was weighed in a titration flask and diluted to 100 ml with distilled water. To this solution, 10 drops of bromocresol green indicator were added. It was titrated with 0.020 M hydrochloric acid (HCl) until the solution turned green. This standard was used as the desired color for the remaining samples. The second standard was titrated in the same manner. Water samples from each site were also titrated in duplicate to the same color as the standard solution using the same procedure without dilution. Additionally, the density was measured for each sample by weighing 100 ml of sample measured in a volumetric flask. The following formula was used to calculate the alkalinity of each sample:

$$\text{Alkalinity} = \frac{500 d V_{bx}}{W V_{bs}}$$

Where d = density of the water sample, V_{bx} = the volume of titrant needed to neutralize the sample, W = weight of the sample and V_{bs} = the volume of the sample needed to neutralize 10 ml of the standard. Weights were used for the analysis because the balance used has higher accuracy than the various pipets, micro-pipets, and flasks used to measure the solutions.

The method described by Rainwater and Thatcher (1960) follows:

Apparatus and Reagents:

- Titration assembly, consisting of pH meter, medium-speed mechanical stirrer, and 50 ml buret.
- Sulfuric acid, 0.01639N, 1.00 ml \approx 1.00 mg HCO_3^-

Procedure:

Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way.

1. Pipet a volume of sample containing less than 40 mg alkalinity as HCO_3^- (50.0 ml max.) into a suitable beaker.
2. Insert beaker in titration assembly and record the pH.

3. Start the stirrer and proceed immediately with the titration.
4. Record the titrant volume at pH 8.2 and 4.5.

Calculations:

$$\text{ppm } \text{HCO}_3^- = \frac{1}{\text{density}} \cdot \frac{1,000}{\text{ml sample}} \cdot [\text{ml titrant (pH 4.5 - pH 8.2)} - (\text{ml pH 8.2})]$$

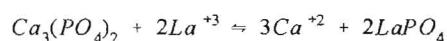
The procedure described by Rainwater and Thatcher (1960) was not used for this study because the approximate alkalinity concentration was unknown at the beginning of the study. This made it difficult to determine the appropriate amounts of solution to use for this method making the use of a color indicator the better choice.

The next analysis determined Ca^{+2} and Mg^{+2} concentrations. This technique is valid for samples collected up to six months earlier. Most of the samples were not kept for the entire allowable holding period. To slow deterioration of samples, they were refrigerated at 4°C.

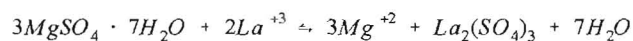
Before testing for Ca^{+2} and Mg^{+2} concentrations (hardness), each water sample was filtered using a glass-fiber filter in order to remove the error of light scattering from suspended particles in the water samples. When the samples are not filtered, small particles suspended in the samples can deflect the light beam from the spectrophotometer, giving abnormally high absorbance readings. This leads to anomalously high values for Ca^{+2} and Mg^{+2} concentration. Each sample was diluted by a 1:16.67 factor for Ca^{+2} and a 1:50 factor

for Mg^{+2} to obtain a concentration within the linear range for this element. The linear range of Mg^{+2} is 0.02 to 0.5 mg/L and the linear range of Ca^{+2} is 0.2 to 6.0 mg/L. Outside of this range, the readings are no longer linear and will give low absorbance readings leading to lower than true concentrations.

To prevent interference of other ions such as sulfate (SO_4^{-2}) and phosphate (PO_4^{-3}), 500 μ l of lanthanum (La^{+3}) was added to each prepared sample. The lanthanum combined with the sulfate to free the calcium in the following way:



The lanthanum was also used in the magnesium samples as shown in the following equation:



Using the Perkin-Elmer model 603 atomic spectrophotometer and the lamp specific to each element, the instrument was calibrated with distilled water. Calibration included settings for light wavelength, burner height, interval time, slit width, lamp current, air flow and fuel flow. These settings were taken from a chart in *Laboratory Manual for Analytical Chemistry* (Schroeder, 1995). The settings were then adjusted until the maximum absorbance, defined as the sensitivity multiplied by the concentration, were found for at least one of the standard solutions. Average settings for each analysis are found below,

although they may be slightly different for every analysis due to small changes in conditions at the time of analysis.

Table 3: Typical Ca^{+2} , Mg^{+2} settings for the Perkin-Elmer 603 spectrophotometer

Element	Wavelength (λ)	Lamp Current (l.c.)	Burner Height (b.h.)	Slit Width (slit)	Air Flow (air)	Fuel Flow (fuel)	Interval Time (int.)
Ca^{+2}	423.7 nm	17 amps	7	0.7	25 pounds /sq. in	15 pounds /sq. in	4 sec
Mg^{+2}	286.2 nm	17 amps	7	0.7	25 pounds /sq. in	15 pounds /sq. in	4 sec

After calibration, each sample was analyzed along with four standard solutions of known concentrations for each element. These standard readings created a calibration curve to which the unknown readings could be compared. Five readings for each unknown were taken during the analysis to reduce error. The settings used in the analysis were also recorded. Using Quattro Pro®, these readings and the standard data were used to calculate the Ca^{+2} and Mg^{+2} concentrations of each sample.

The methods described in Rainwater and Thatcher (1960) for Ca^{+2} were not used in this study. The reasons why are in the following table.

Table 3: Reasons for not using USGS Ca⁺² determinative methods

Complexometric Method	A photometric-titration assembly was not available
Permanganimetric Method	Interference by Mg ⁺² ions
Gravimetric Method	Normally used in the analysis of brines, acid waters and concentrated industrial waste
Turbidimetric Method	Only semi-quantitative. Useful in fieldwork for determining the proper sample volume for quantitative determination.

The methods described in Rainwater and Thatcher (1960) for Mg⁺² were also not used in this study. The reasons for this decision are in the following table:

Table 4: Reasons for not using USGS Mg⁺² determinative methods

Calculation Method	Complexometric method was not used for Ca ⁺²
Pyrophosphate Method	Used in the analysis of brines, acid waters and concentrated industrial wastes.
Eriochrome Black T Method	Not applicable for Mg ⁺² over 100 ppm. In the beginning of this study, approximate concentrations were unknown.

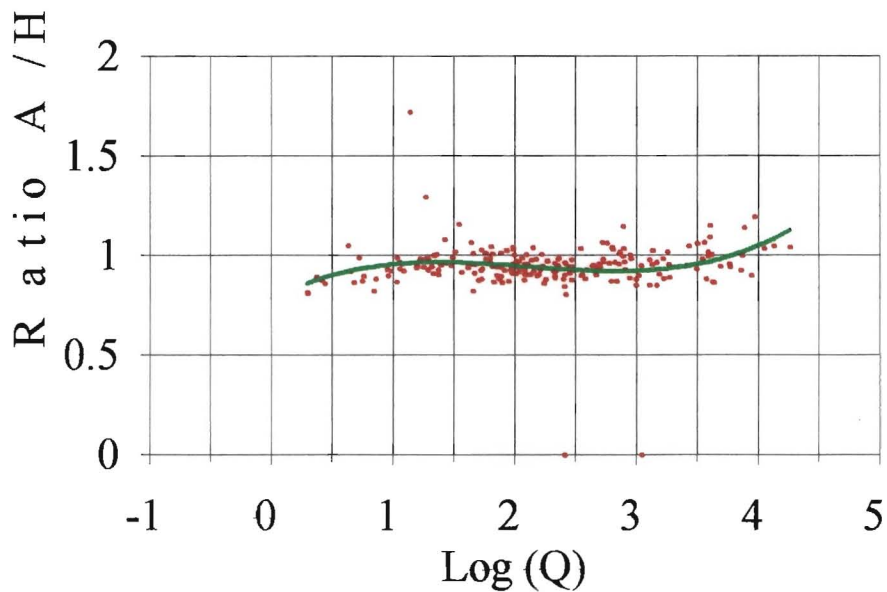
DISCUSSION

The data collected from the sites along the Marais de Cygnes River indicates a subtle relationship between the A/H ratio and the discharge of the river at Site 1. The trend from 30 years ago (figure 7) shows the regression sloping in a positive direction as discharge increases. As shown by the linear regression (figure 8), as the discharge increases, the ratio decreases. This positive relationship is also shown in the previous data at Site 2 (figure 9), but not in the regression for the current data (figure 10). The regulation of the discharge from Melvern Dam is likely responsible for this absence of the negative relationship.

Comparison of the current ratio of alkalinity to hardness (A/H) by month shows dips in the ratio (figure 11). They are in March and June with a second, less distinct depression is in November. These changes may be related to variations in discharge. It is common for slight acidification to occur in March due to spring melting of accumulated precipitation. This is known as “spring acid shock”. June precipitation was normal to high, and end-of-May discharge was roughly 5 times higher than normal, which may have affected concentrations found in the June data. Alkalinity values for June are in line with other values for alkalinity in other months, however the values for Ca^{+2} and Mg^{+2} are higher than normal, lowering the ratio. In November, precipitation was also high and the

Site 1 1964 - 68

Discharge versus Ratio A/H



• Observed Ratio — Regression

Figure 7: Discharge versus Ratio A/H, Site 1, 1964 - 1968

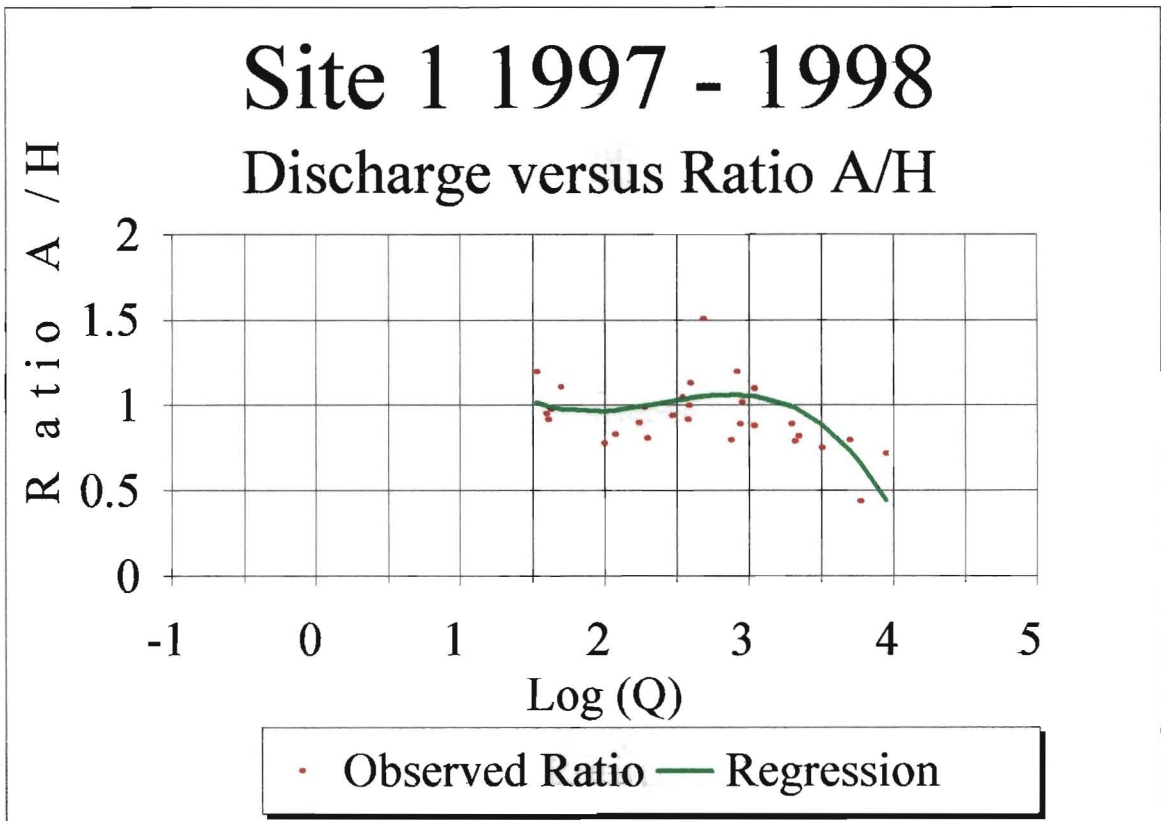


Figure 8: Discharge versus Ratio A/H, Site 1, 1997 - 1998

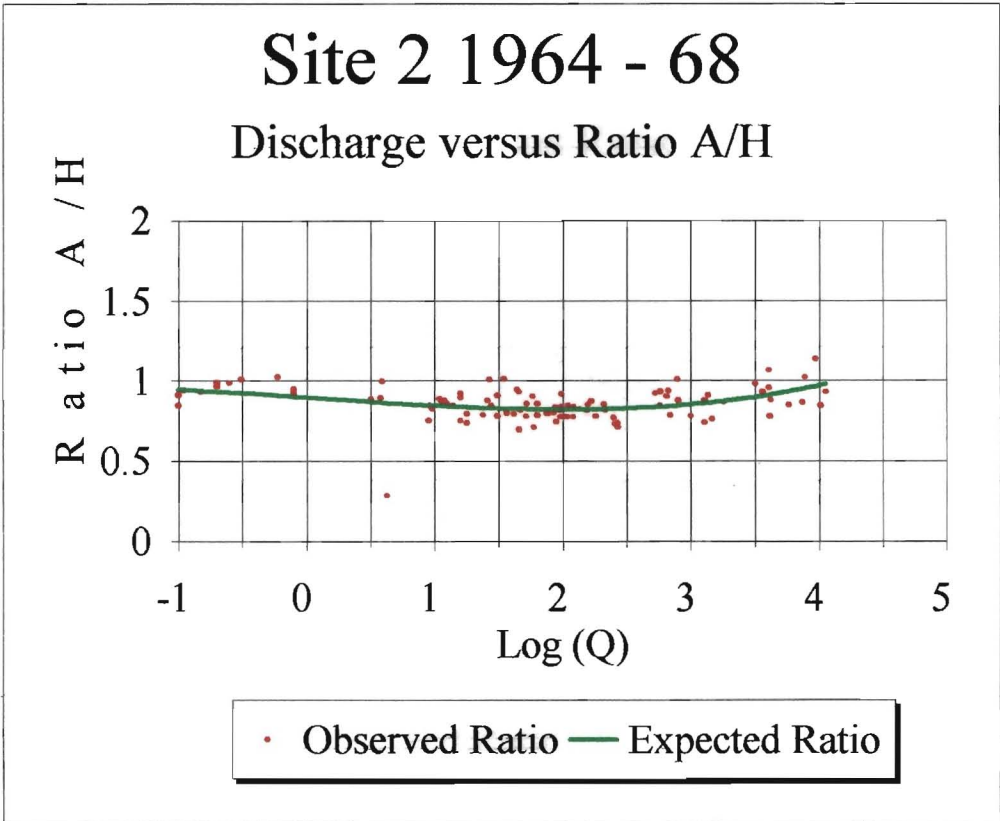


Figure 9: Discharge versus Ratio A/H, Site 2, 1964 - 1968

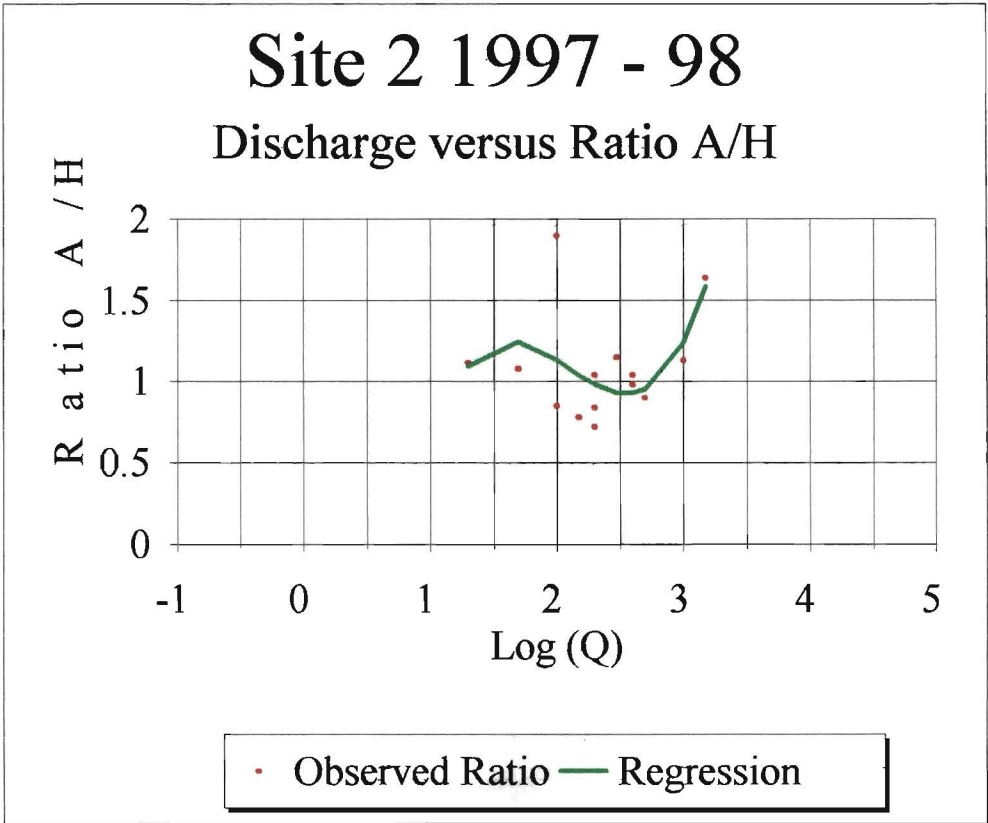


Figure 10: Discharge versus Ratio A/H, Site 2, 1997 - 1998

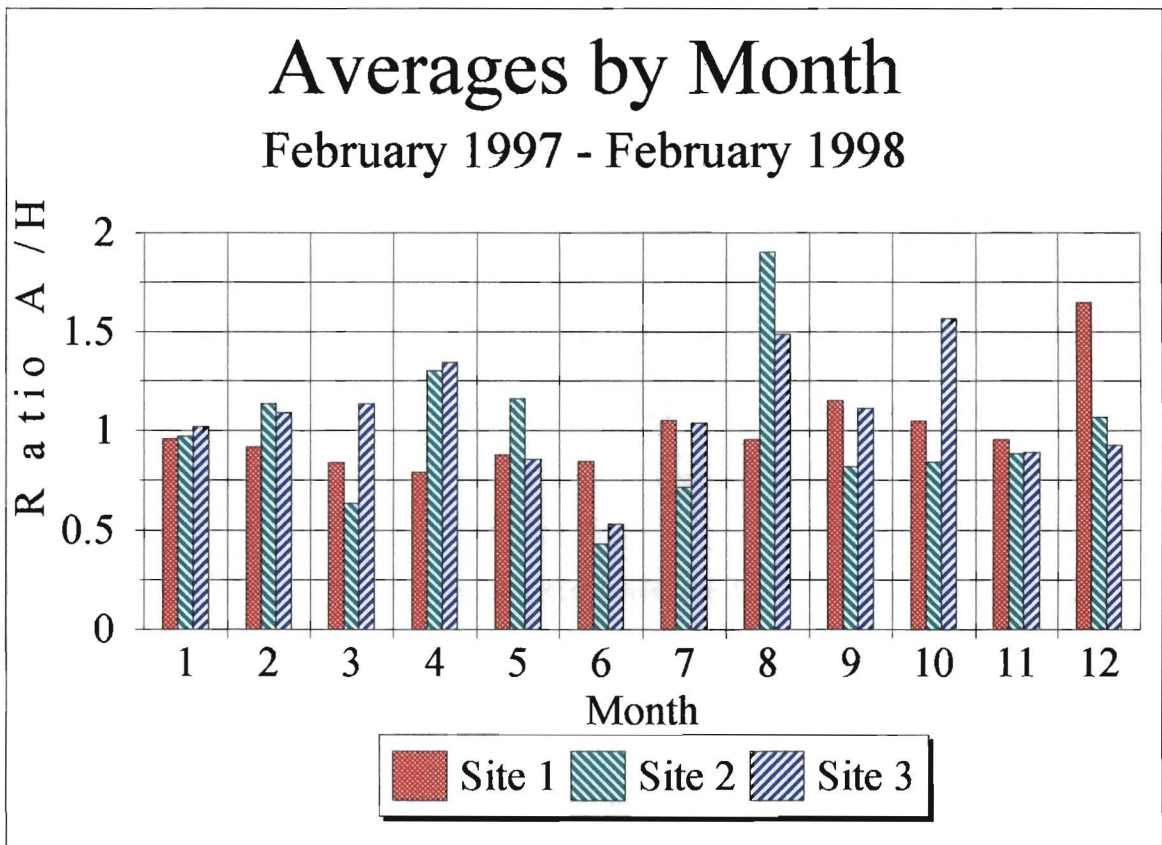


Figure 11: Ratio A/H of All Sites by Month, 1997 - 1998

concentrations of Ca^{+2} and Mg^{+2} are lower, however, the change in alkalinity is not as pronounced, leading to a lowering of the ratio.

A dip in the ratio is also seen in April of the 1960s data for Site 1 and Site 2. This may have also been caused by “spring acid shock” causing temporary acidification of surface waters during the spring melting of accumulated winter precipitation.

Site 3 was used as a proxy sampling site for the conditions of the river at Site 1 and Site 2 that existed over 30 years ago. If the assumption that Site 3 would be able to yield data that mimicked the conditions of the river 30 years ago was correct, the relationship should show a positive relationship between Sites 1 & 2 to Site 3. A comparison of Site 1 to Site 3 (figure 13) and Site 2 to Site 3 (figure 14) does not show this relationship between the present Site 3 and earlier Site 1 or Site 2 data. Therefore, the assumption of a proxy may be false.

There is a large time interval between when the USGS data was collected and the data was gathered for this study. This span of time, approximately 30 years, gave the river a chance to change, although it did not change dramatically apart from the development of Ottawa and Melvern Dam. There are several years of data available for two of the sites from the 1960s providing baseline data to which to compare current findings and these multiple sites allowed for monitoring of several stretches of the river. Nevertheless, this length of time makes trends difficult to evaluate or to determine if the year of the study was normal versus unusual in any way. To overcome these uncertainties, the area should

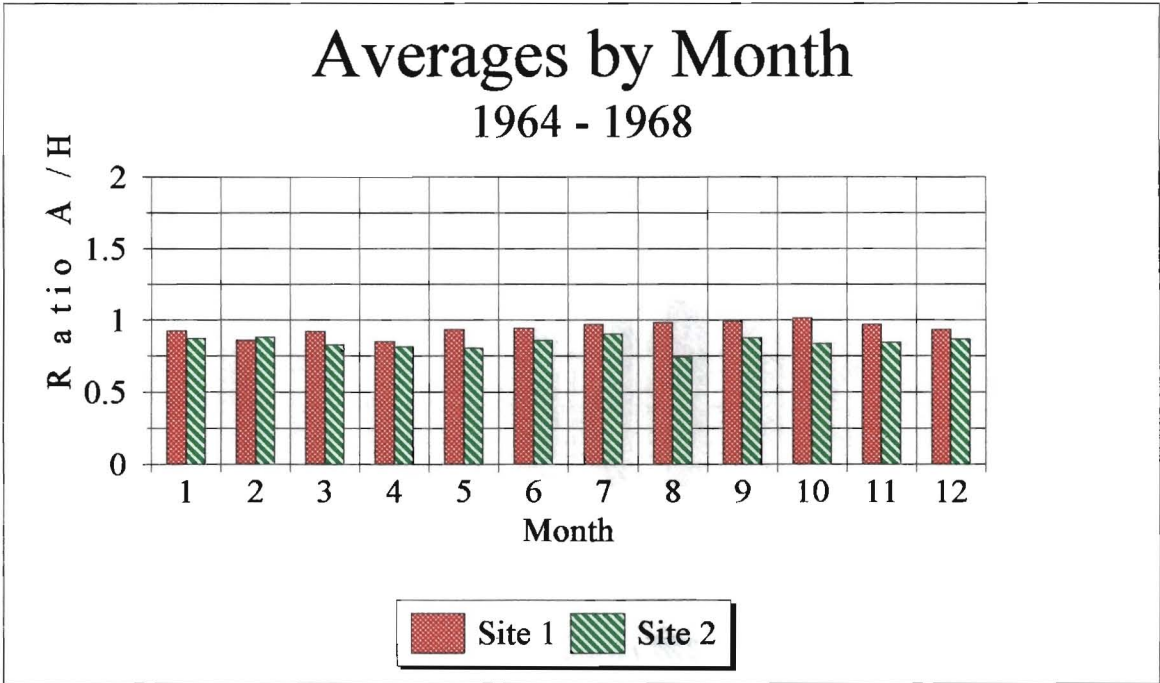


Figure 12: Ratio A/H of All Sites by Month, 1964 - 1968

Site 3 (present) versus Site 1 (past) Monthly Ratios

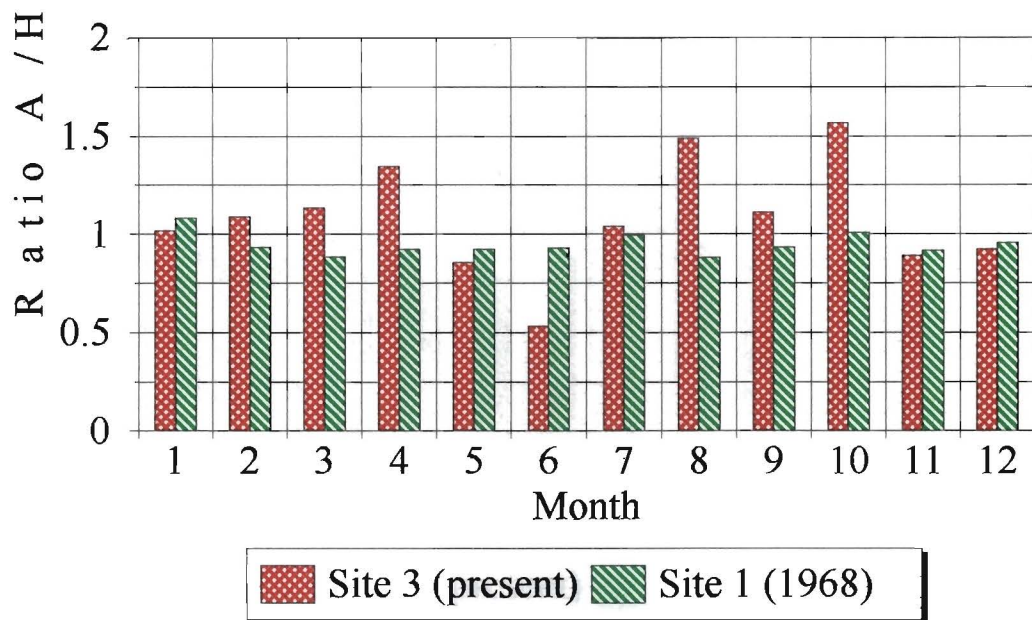


Figure 13: Site 3 (present) ratio A/H versus Site 1 (past) ratio A/H

Site 3 (present) versus Site 2 (past) Monthly Ratios

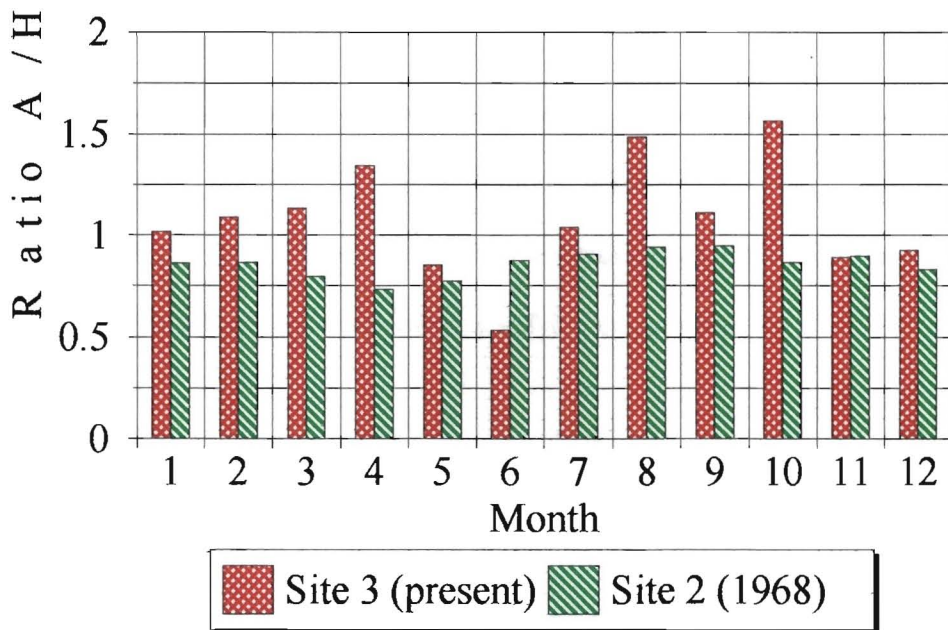


Figure 14: Site 3 (present) ratio A/H versus Site 2 (past) ratio A/H

continue to be sampled for a longer span of time. This would create a current data set with a history of normal patterns and trends to compare to past data.

If this project continued, sulfate (SO_4^{-2}) should be added to the ions for which testing is done. Sulfate is the major acid contributing ion found in acidified water (Likens et al., 1996). Just as the ratio of alkalinity versus hardness decreases as water acidifies, the ratio of sulfate versus hardness typically increases as water acidifies if the acidification is due to acid deposition. This would serve as a check on the alkalinity/hardness ratio and pH measurements.

Another ion that should be added to the study if it were to continue is aluminum (Al) because as water acidifies, Al concentrations generally increase (Lahermo, 1991). According to Lahermo (1991) "Elevated Al concentrations are generally considered to be one of the most harmful consequences of an acidifying environment".

In doing this project, some data had to be disregarded. The data and reasons are as follows:

- The alkalinity data for all Sites on 3/20/97 and 6/17/97 is missing due to an error in measurement of the standard. This error gave incredibly high measurements for V_{bs} . The 24 hour holding period for the sample had expired before the mistake was found. Ratios for those dates cannot be calculated because of this.
- Ca^{+2} measurements are missing for 2/10/97 (Site 1, Site 2 and Site 3) and 6/17/97 (Site 2) because the dilution of the sample was outside the linear range for Ca^{+2} and

the holding time expired before it was reanalyzed. Ratios for those dates cannot be calculated because of this.

- Mg^{+2} measurements are missing for 2/10/97 (Site 1, Site 2, and Site 3), 4/11/97 (Site 2), 4/18/97 (Site 2) and 6/17/97 (Site 2) because the dilution of the sample was outside the linear range for Mg^{+2} and the holding time expired before it was reanalyzed. Ratios for those dates cannot be calculated because of this.
- pH readings for all Sites on 10/14/97, 12/19/97 and 2/17/98 are unavailable because the pH meter was fluctuating wildly and later stopped working altogether. The 2 hour holding period had expired before another pH meter was available.

The purpose of this study was to determine if the water chemistry of the Marais de Cygnes River had changed in the past 30 years and if these changes could be attributed to the problem of acid deposition. This study also hypothesized that Site 3 would stand as a proxy for Site 1 and Site 2 from 30 years ago allowing comparison of the water quality above and below Melvern Dam.

The data collected in this study the ratio of alkalinity versus hardness has not decreased noticeably since the 1960s. However, at high discharge, especially discharge over 1000 cubic feet per second (cfs), the ratio does begin to decrease. Because of this lowering of the ratio as discharge increases, an influx of acid during episodes of precipitation is indicated. However, since the precipitation over this area was not tested as well, acid deposition cannot be said to be the sole cause of this acidification. It is possible that acid is

also being added from other sources such as anthropogenic pollution in Ottawa or organic acids leaching into the water from the soil.

Finally, the data collected does not bear out the hypothesis that Site 3 stands as a proxy for Site 1 and Site 2 from the 1960s. No relationship was seen between Site 3 and either Site 1 or Site 2. Due to this, a comparison of water quality upstream and downstream from Melvern Dam was not possible.

The Marais de Cygnes River is being acidified at high discharge compared to 30 years ago. However, because the precipitation for this region was not tested, this study is not able to conclusively say that this acidification is due entirely to acid deposition. The lowering of the ratio during high discharge points to acid being added during times of precipitation, but a study of acid content in precipitation is recommended before stating this definitively. This study is also unable to state what effect, if any, Melvern Dam has had upon the acidification of the river since Site 3 was rejected as a proxy for Site 1 and Site 2 from 1964 - 68. The dam was only shown to have a buffering effect on the ratio, probably due to the holding time in Melvern Lake.

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Appendix A

Data

<u>Date</u>	<u>Discharge</u>	<u>Water temp</u>	<u>Air Temp</u>	<u>pH 4</u>	<u>pH 7</u>	<u>Obs. pH</u>	<u>True pH</u>	<u>Alk 1</u>	<u>Alk 2</u>	<u>Alkalinity</u>	<u>Ca+2</u>	<u>Mg+2</u>	<u>Observed Ratio</u>
02/10/97	130	0.00	4.50	4.67	7.87	8.67	8.41	2.22	2.22	2.22	—	—	—
02/14/97	120	1.50	12.00	4.58	7.80	8.35	8.08	3.83	3.83	3.83	3.19	1.45	0.83
02/21/97	6000	5.50	4.50	4.60	7.61	7.41	7.26	1.57	1.59	1.58	2.12	1.50	0.44
02/28/97	2100	4.00	8.50	4.29	7.43	8.01	8.15	2.45	2.48	2.46	2.33	0.77	0.79
03/07/97	2250	6.50	13.00	4.86	7.81	8.33	8.10	2.75	2.76	2.75	2.23	1.11	0.82
03/14/97	764	6.00	1.50	3.19	5.99	7.10	8.88	2.94	2.94	2.94	2.42	1.27	0.80
03/20/97	171	10.50	22.00	3.98	7.26	7.49	7.71	—	—	—	3.12	1.93	—
03/31/97	175	15.00	24.00	4.06	7.27	8.18	8.42	4.26	4.19	4.22	3.41	1.30	0.90
04/11/97	9000	4.00	3.20	3.79	6.96	6.67	7.28	1.67	1.69	1.68	1.49	0.83	0.72
04/18/97	3250	10.00	21.00	4.47	7.75	7.00	6.68	2.84	2.87	2.85	2.31	1.49	0.75
04/25/97	2000	12.00	15.00	4.13	7.36	7.63	7.75	2.77	2.74	2.75	2.39	0.71	0.89
05/02/97	190	14.50	18.00	3.63	7.22	6.79	7.04	3.53	3.47	3.50	2.60	0.94	0.99
05/09/97	300	17.50	17.00	4.01	7.51	7.74	7.66	4.05	4.08	4.07	3.61	0.73	0.94
05/17/97	100	25.00	32.50	3.67	7.40	8.95	8.83	3.66	3.67	3.66	2.88	1.84	0.78
05/31/97	5000	17.00	23.00	3.22	6.76	8.79	9.41	2.05	2.13	2.09	2.03	0.59	0.80
06/07/97	1100	21.50	25.50	4.82	8.21	8.68	7.90	2.94	2.94	2.94	2.51	0.84	0.88
06/17/97	1500	24.00	30.00	4.65	8.14	8.46	7.73	—	—	—	2.42	0.91	—
06/30/97	200	28.00	31.00	4.74	8.18	9.87	9.07	3.28	3.31	3.29	2.91	1.14	0.81
07/12/97	1100	26.00	32.00	5.03	8.66	9.22	7.93	2.83	2.87	2.85	2.24	0.36	1.10
07/20/97	400	27.50	26.00	3.96	7.54	8.15	7.41	3.09	3.10	3.10	2.25	0.48	1.13
07/29/97	381	27.00	30.00	3.57	7.45	8.63	8.44	3.18	3.10	3.14	2.47	0.94	0.92
08/31/97	40	25.50	26.00	4.46	8.16	8.79	7.99	2.87	2.77	2.82	2.37	0.59	0.95
09/06/97	34	27.50	28.00	4.70	8.49	9.79	8.57	3.01	3.02	3.02	2.08	0.44	1.20
09/15/97	50	26.50	30.00	3.09	6.82	7.85	8.35	3.34	3.33	3.34	2.55	0.47	1.11
10/14/97	350	—	—	—	—	—	—	2.86	2.69	2.78	2.12	0.53	1.05
11/04/97	43	10.00	8.00	4.76	8.31	8.90	8.05	3.75	3.95	3.85	3.18	0.74	0.98
11/18/97	41	5.00	4.00	4.25	6.33	7.45	9.38	3.95	4.02	3.98	3.38	0.93	0.92
12/02/97	751	15.50	8.50	4.43	7.74	8.53	8.27	2.42	2.45	2.44	1.14	0.02	2.10
12/19/97	835	4.00	2.00	—	—	—	—	3.05	3.01	3.03	2.03	0.50	1.20
01/20/98	905	1.00	2.00	3.67	6.69	6.76	7.60	2.95	2.94	2.95	2.28	0.62	1.02
01/27/98	872	4.00	2.50	3.53	6.70	6.82	7.64	2.92	3.09	3.01	2.66	0.70	0.89
02/03/98	490	2.00	0.00	4.30	7.63	7.57	7.45	6.98	6.86	6.92	3.65	0.92	1.51
02/17/98	391	—	—	—	—	—	—	3.15	3.14	3.15	2.43	0.71	1.00

Date	Discharge	Water temp	Air Temp	pH 4	pH 7	Obs. pH	True pH	Alk 1	Alk 2	Alkalinity	Ca+2	Mg+2	Observed Ratio
02/10/97	20	2.00	-1.00	4.98	8.19	9.00	8.40	1.98	1.98	1.98	—	—	—
02/14/97	20	2.50	11.00	4.47	7.71	8.65	8.53	2.56	2.54	2.55	1.62	0.79	1.06
02/21/97	20	3.50	2.00	4.20	7.41	7.58	7.69	2.16	2.08	2.12	1.52	0.73	0.94
02/28/97	300	4.00	10.00	4.39	7.53	9.60	9.81	2.57	2.54	2.55	1.61	0.61	1.15
03/07/97	1000	5.50	11.50	4.60	7.60	7.97	7.93	2.61	2.63	2.62	1.63	0.68	1.13
03/14/97	50	9.00	-2.00	3.19	5.99	7.59	9.46	2.50	2.71	2.60	1.68	0.72	1.08
03/20/97	20	10.50	24.00	4.07	7.34	7.93	8.09	—	—	—	1.71	0.67	—
03/31/97	20	13.00	21.50	4.25	7.59	7.90	7.78	2.68	2.69	2.69	1.71	0.68	1.12
04/11/97	20	5.50	1.50	3.10	7.01	7.06	7.55	2.50	2.49	2.49	1.49	—	1.67
04/18/97	1500	13.00	22.00	4.34	7.70	7.89	7.65	2.68	2.67	2.67	1.63	—	1.64
04/25/97	500	10.00	16.50	3.72	7.36	7.30	7.41	2.64	2.64	2.64	2.27	0.67	0.90
05/02/97	20	12.00	16.00	4.25	7.31	6.91	7.01	2.79	2.76	2.78	2.46	0.77	0.86
05/09/97	20	13.50	15.00	4.37	7.61	8.06	7.93	2.66	2.63	2.65	2.43	0.55	0.89
05/17/97	20	20.00	30.50	3.89	7.63	7.89	7.66	2.73	2.74	2.73	2.21	0.97	0.86
05/30/97	100	19.00	25.50	4.50	6.70	8.63	10.44	2.67	2.59	2.63	2.30	0.78	0.85
06/07/97	20	29.50	29.50	4.45	7.92	8.36	7.83	2.68	2.63	2.65	2.46	0.71	0.84
06/17/97	20	20.00	30.00	4.49	6.69	8.11	9.64	—	—	—	—	—	—
06/30/97	20	24.00	29.50	4.47	7.31	10.10	10.76	2.73	2.88	2.80	3.72	1.78	0.51
07/12/97	20	23.00	29.50	4.94	8.55	9.00	7.84	2.92	2.98	2.95	2.26	0.41	1.10
07/20/97	200	20.00	28.00	3.97	7.53	7.83	7.72	3.12	3.10	3.11	3.04	1.27	0.72
07/29/97	200	20.50	34.00	3.29	6.99	7.05	7.48	2.97	2.99	2.98	2.21	1.33	0.84
08/31/97	20	20.00	27.00	4.14	7.94	8.12	7.59	3.24	3.22	3.23	2.48	0.94	0.95
09/06/97	20	24.00	30.00	4.46	8.26	8.72	7.83	2.88	2.90	2.89	2.22	0.43	1.09
09/15/97	20	24.50	31.00	3.07	6.35	7.26	8.36	3.35	3.32	3.33	1.83	0.47	1.45
10/14/97	20	—	—	—	—	—	—	2.61	2.65	2.63	2.06	0.71	0.95
11/04/97	20	12.00	11.50	4.41	7.89	8.90	8.46	2.70	2.68	2.69	1.91	0.58	1.08
11/18/97	20	7.00	6.00	4.09	6.20	7.51	9.65	2.65	2.69	2.67	1.91	0.60	1.06
12/02/97	20	17.00	10.50	4.15	7.47	8.66	8.67	2.72	2.65	2.69	1.90	0.62	1.07
12/19/97	200	5.00	7.00	—	—	—	—	2.77	2.69	2.73	2.00	0.63	1.04
01/20/98	400	2.00	5.00	3.52	6.85	6.76	7.42	2.55	2.57	2.56	2.04	0.56	0.98
01/27/98	400	4.00	4.00	3.72	6.54	6.55	7.52	2.63	2.70	2.67	1.95	0.61	1.04
02/03/98	100	1.00	0.50	4.05	7.05	7.75	8.34	5.32	5.28	5.30	2.03	0.76	1.90
02/17/98	150	—	—	—	—	—	—	2.48	2.48	2.48	2.39	0.79	0.78

Data for Site 2, 1997 - 98

<u>Date</u>	<u>Water temp</u>	<u>Air Temp</u>	<u>pH 4</u>	<u>pH 7</u>	<u>Obs. pH</u>	<u>True pH</u>	<u>Alk 1</u>	<u>Alk 2</u>	<u>Alkalinity</u>	<u>Ca+2</u>	<u>Mg+2</u>	<u>Observed Ratio</u>
02/10/97	0.00	-2.00	4.77	8.46	8.93	7.98	2.57	2.59	2.58	—	—	—
02/14/97	2.00	12.50	4.69	7.95	8.44	8.05	4.35	4.42	4.39	3.78	1.47	0.84
02/21/97	5.00	3.00	4.77	7.64	7.70	7.57	1.79	1.79	1.79	1.55	0.67	0.81
02/28/97	4.50	13.00	5.46	8.44	9.09	8.26	3.70	3.70	3.70	2.46	1.16	1.02
03/07/97	5.50	10.30	4.64	7.85	8.27	7.95	4.87	4.67	4.77	2.97	1.31	1.11
03/14/97	6.50	1.50	3.19	5.99	7.89	9.86	5.25	5.24	5.24	3.16	1.45	1.14
03/20/97	9.00	24.50	3.92	7.27	8.12	8.36	—	—	—	1.85	1.46	—
03/28/97	13.50	21.30	4.33	7.74	8.32	8.04	5.22	5.26	5.24	2.78	1.79	1.15
04/11/97	3.00	3.80	3.72	6.92	6.88	7.47	1.56	1.60	1.58	1.20	0.16	1.16
04/18/97	16.00	21.00	4.43	7.82	7.49	7.11	5.09	5.10	5.10	3.14	0.34	1.46
04/25/97	13.00	15.50	4.08	7.37	7.78	7.89	5.80	5.80	5.80	2.57	1.56	1.40
05/02/97	15.00	18.00	4.18	7.61	6.38	6.21	5.55	5.58	5.56	4.21	1.50	0.97
05/09/97	16.00	15.00	4.06	7.35	7.43	7.53	2.13	2.10	2.12	2.08	0.44	0.84
05/17/97	23.50	35.50	3.88	7.36	8.14	8.18	5.10	5.11	5.11	4.69	1.82	0.78
05/30/97	19.00	22.00	4.59	8.12	8.49	7.79	2.80	2.82	2.81	2.49	0.96	0.81
06/07/97	30.50	33.50	4.60	7.97	9.08	8.51	4.24	4.31	4.28	12.20	1.55	0.31
06/17/97	30.50	33.50	4.83	8.28	9.23	8.33	—	—	—	2.65	1.09	—
06/30/97	31.50	32.50	4.72	8.13	8.10	7.37	4.51	4.47	4.49	4.40	1.55	0.75
07/12/97	27.00	31.00	4.46	7.99	8.64	8.03	3.01	2.97	2.99	2.16	0.96	0.96
07/20/97	29.00	32.00	4.26	7.90	8.46	9.21	3.59	3.52	3.55	2.16	0.54	1.32
07/29/97	31.50	36.00	4.92	8.62	9.02	7.76	2.46	2.46	2.46	2.21	0.71	0.84
08/31/97	26.00	29.00	4.41	8.26	8.43	7.56	3.22	3.09	3.15	1.32	0.80	1.49
09/06/97	27.00	32.50	3.93	7.73	8.31	7.92	3.41	3.36	3.39	2.51	0.63	1.08
09/15/97	27.50	33.50	4.43	7.66	9.31	9.14	3.69	3.83	3.76	2.63	0.66	1.14
10/14/97	—	—	—	—	—	—	2.71	2.71	2.71	1.03	0.70	1.57
11/04/97	9.00	14.00	4.42	7.76	8.04	7.48	2.68	2.61	2.65	2.46	0.74	0.83
11/18/97	4.00	6.00	4.41	6.46	7.40	9.11	4.31	4.31	4.31	3.50	1.03	0.95
12/02/97	15.50	11.50	4.38	7.73	8.39	8.12	2.86	2.97	2.92	2.65	1.39	0.72
12/19/97	8.00	3.50	—	—	—	—	4.02	4.03	4.03	2.64	0.94	1.12
01/20/98	1.00	6.00	3.68	6.92	7.12	7.74	5.57	5.60	5.59	3.96	1.30	1.06
01/27/98	4.00	6.00	4.02	6.38	6.29	7.37	5.77	5.71	5.74	4.39	1.52	0.97
02/03/98	2.00	1.00	4.64	6.64	6.45	7.62	8.68	8.64	8.66	3.81	1.43	1.65
02/17/98	—	—	—	—	—	—	5.01	5.21	5.11	3.47	1.07	1.13

Data for Site 3 1997 - 98

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Kimberly Hanson

Signature of Author

May 8, 1998

Date

Changes in the Surface Water of the
Marais de Cygnes River, 1964 to 1968.

Title of Thesis

Doug Cooper

Signature of Graduate Office Staff

May 8, 1998

Date Received

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