# WATER CHEMISTRY OF BREWSTER LAKE, PIERCE CEDAR CREEK INSTITUTE

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#### INTRODUCTION

Seven properties of the water of Brewster Lake and Cedar Creek were measured as indicators of the quality of water flowing through Pierce Cedar Creek Institute (PCCI) lands. Our work provides a detailed description of the local water chemistry which may be of considerable use to others engaged in research at the site. Questions we wished to address included: Is the water chemistry of PCCI affected by nearby agriculture or other human activity? How does the water chemistry of PCCI compare to that of similar environments, in Michigan and elsewhere? Does precipitation measurably affect the water chemistry of PCCI? Is the water chemistry uniform or does it vary geographically? How does the water composition vary between May and July?

#### **MATERIALS & METHODS**

All ordinary glassware and Nalgene bottles used during our research were washed with non-phosphate soap (Palmolive dishwashing liquid) and then rinsed with 0.1 M HCl, followed by rinses with water serially purified by a Besco water deionizer and a Barnstead Nanopure system.

Standard analytical methods, approved by the United States Environmental Protection Agency (EPA) and/or the Association of Official Analytical Chemists (AOAC), were used to measure chemical and physical properties of the waters of Brewster Lake and Cedar Creek. Water temperature, pH, and dissolved oxygen were measured on site during the sampling operation. Analyses of total alkalinity, phosphates, nitrates, and conductivity were performed in the Chemistry Department of Aquinas College.

A total of 22 sites were selected around the perimeter of Brewster Lake. These sites were roughly 30 meters apart and followed the contours of the shoreline. Sampling was done from a boat anchored as close as possible to the shore and always from the side nearest to the center of the lake. Two sites along Cedar Creek (designated 1-B and 2-B) were added 20 June (see attached map). Water was collected from the top ~ 30 cm of the lake in acid-washed 500 mL Nalgene bottles (EPA, 1997) by inserting the open bottle vertically (mouth upward) into the water and holding it there until all of the air had escaped from the bottle. Water samples were stored on ice until analysis was complete.

Water samples were collected once per week for nine weeks (22 May through 17 July). After the initial sample collection, odd- and even-numbered lake sites were sampled on alternate weeks; both creek sites were sampled every week beginning 20 June. Samples from sites 10 and 11 (22 May) and sites 8 and 1-B (29 May) which had high turbidity

were filtered with suction through 30-mL, medium porosity, sintered glass filtering crucibles before laboratory analyses.

### Alkalinity

A potentiometric method was used to determine alkalinity (Greenberg, et al). Before every use, the pH probe was calibrated against commercial pH 4.00, 7.00, and 10.00 buffer solutions. A 0.1 M HCl solution was standardized potentiometrically against anhydrous primary standard Na<sub>2</sub>CO<sub>3</sub>. When the pH was near 5, the sample was boiled for 3-5 minutes and allowed to cool before continuing the titration to the equivalence point.

Using a 50.00 mL volumetric pipette, 250.00 mL of each water sample was transferred to a beaker. The aliquot was titrated with the standard HCl until the pH was approximately 4.6. The water alkalinity was calculated from the volume of acid required to reach this point.

### **Conductivity**

Conductivity was measured with a Fisher Scientific Digital Conductivity Meter with automatic temperature compensation. A standard solution of KCl (0.7355 g of anhydrous KCl dissolved in 1000.0 mL water) was referenced before each set of measurements and the reading set to 1412  $\mu$ mho/cm. To measure sample conductivity, the probe was placed directly into the sample bottle. The reading was taken after stirring the probe gently in the solution for 15 seconds.

## **Dissolved Oxygen**

Dissolved oxygen was measured at the sampling sites using a Milwaukee SM600 dissolved oxygen meter, owned by the Aquinas College Biology Department. The probe was calibrated at the beginning of the project. Readings were collected after submerging the probe about two to three inches into the lake at each site for 15 seconds. Dissolved oxygen was not measured for any site during the final week of the study (17 July).

### **Nitrates**

The nitrate levels of Brewster Lake were found using an ultraviolet spectrophotometric method (Greenberg, et al). The absorbance of each water sample was measured on a WPA Lightwave S2000 diode-array spectrophotometer at 220 nm. The instrument light source was always given at least thirty minutes to warm up before any measurement. The concentration of nitrates determined was not corrected for possible interference by organic materials or other nitrogen-containing species.

A 50.0 mL aliquot of each water sample was pipetted into a 100 mL beaker. To each sample, 1.0 mL of 1 M HCl was added using a volumetric pipette. Every week a set of five standards were prepared volumetrically from a stock nitrate solution (0.7218 g dried KNO<sub>3</sub> in water, 1000.0 mL total volume). The nitrate standards for the first three weeks had nitrate concentrations between 14 ppm and 146 ppm. After finding that all samples fell between 14 ppm and 29 ppm nitrate, an additional standard was inserted between

these concentrations and the highest two standard solutions were omitted. The standard solutions were treated in the same manner as the water samples before measurement.

### pH and Temperature

The pH and temperature were measured on-site with a Fisher Scientific Accumet AP62 portable pH/mV meter, calibrated weekly against commercial pH 4 and pH 10 buffer solutions.

### **Phosphates**

Phosphate levels were determined by the ascorbic acid method using a Beckman DU-64 spectrophotometer with quartz cuvets (Greenberg, et al). A 50.00 mL aliquot of each water sample was transferred to a clean, dry 125-mL Erlenmeyer flask, and one drop of phenolphthalein indicator solution was added. If the sample developed a pink tinge, 5 M sulfuric acid was added to the solution dropwise until it returned to a colorless state. Eight mL of the combined reagent was then added to each sample and the absorbance of the solution at 880 nm was measured between 10 and 30 minutes after the addition.

The combined reagent was a mixture of 100 mL of 5 M aqueous sulfuric acid, 10 mL potassium antimonyl tartrate solution (1.3684 g K(SbO)C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.½ H<sub>2</sub>O in water, 500.0 mL total volume), 30 mL ammonium molybdate solution (20 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4 H<sub>2</sub>O in water, 500.0 mL total volume), and 60 mL of fresh ascorbic acid solution (1.76 g ascorbic acid in water, 100.0 mL total volume; prepared weekly).

Six standard phosphate solutions were prepared volumetrically each week from a stock phosphate solution (50 mg  $PO_4^{3-}$  per L, made from anhydrous  $KH_2PO_4$ ). Treatment of the standard solutions prior to absorbance measurement was the same as for the water samples.

#### **RESULTS & DISCUSSION**

# **Alkalinity**

The alkalinity generally decreased throughout the summer (see Table 1). All sites' alkalinity levels were within a few parts per million of each other each week. The mean alkalinity of the lake sites decreased by 3–8 ppm CaCO<sub>3</sub> each week except the second (29 May) and seventh (5 July) weeks of the study, in which the alkalinity increased by 3 ppm CaCO<sub>3</sub> over the previous week.

The sites along Cedar Creek always had higher alkalinity than the lake mean for the same week. Site 2-B was always significantly higher than site 1-B, except on 5 July when the alkalinity of site 1-B was 380.23 ppm CaCO<sub>3</sub>, the highest level recorded during the study. Neither of the creek sites showed decreasing alkalinity comparable to the lake trend; they were more or less constant. The range for 1-B was 175–195 ppm CaCO<sub>3</sub> (not including the exceptionally high value mentioned above) and the range for 2-B was 228–254 ppm CaCO<sub>3</sub>.

Table 1. Mean alkalinity (ppm CaCO<sub>3</sub>) of Brewster Lake sites.

| Date         | Mean   | Standard Deviation | No. of Samples |
|--------------|--------|--------------------|----------------|
| 22 May 2005  | 188.93 | 7.4                | 15             |
| 29 May 2005  | 191.71 | 0.75               | 11             |
| 5 June 2005  | 184.11 | 4.9                | 11             |
| 12 June 2005 | 178.70 | 6.8                | 11             |
| 20 June 2005 | 175.20 | 2.8                | 11             |
| 26 June 2005 | 167.77 | 8.5                | 10             |
| 5 July 2005  | 170.70 | 6.0                | 11             |
| 10 July 2005 | 167.71 | 4.9                | 11             |
| 17 July 2005 | 159.38 | 3.8                | 11             |

# **Conductivity**

The conductivity of Brewster Lake decreased steadily during the summer (see Table 2), from an average of 357  $\mu$ mho/cm (22 May) to 269  $\mu$ mho/cm (17 July). The readings taken each week from the lake were fairly similar with an average range of 37  $\mu$ mho/cm. However the conductivity of water taken from the creek sites was always higher than the average lake conductivity, and site 2-B was always about 100  $\mu$ mho/cm higher than site 1-B. Both creek sites' conductivities decreased although a small increase was noted at both sites after reaching a minimum on 5 July. The mean conductivity (over all weeks measured) was 301, 321, and 424  $\mu$ mho/cm for the lake sites, site 1-B, and site 2-B, respectively.

Table 2. Mean conductivity (µmho/cm) of Brewster Lake sites.

| Date         | Mean | <b>Standard Deviation</b> | No. of Samples |
|--------------|------|---------------------------|----------------|
| 22 May 2005  | 357  | 10.6                      | 22             |
| 29 May 2005  | 339  | 9.0                       | 11             |
| 5 June 2005  | 308  | 7.2                       | 11             |
| 12 June 2005 | 315  | 9.5                       | 11             |
| 20 June 2005 | 311  | 11.0                      | 11             |
| 26 June 2005 | 280  | 15.4                      | 11             |
| 5 July 2005  | 263  | 13.1                      | 11             |
| 10 July 2005 | 265  | 9.8                       | 11             |
| 17 July 2005 | 269  | 12.1                      | 11             |

### **Dissolved Oxygen**

The dissolved oxygen concentration decreased regularly for all lake sites from about 9 mg/L to about 5 mg/L (see Table 3). Sites 1-B and 2-B dropped from about 5 mg/L to as low as 3.7 mg/L. The creek sites had lower levels of dissolved oxygen than any of the lake sites, and this remained true throughout the study period.

It is possible that the decrease in dissolved oxygen in the water samples could be due to increased microbial and/or plant life in the lake as the temperature increased. A dramatic explosion of plant growth in and around the lake was observed during the study.

Table 3. Mean dissolved oxygen (mg/L) of Brewster Lake sites.

| Date         | Mean | <b>Standard Deviation</b> | No. of Samples |
|--------------|------|---------------------------|----------------|
| 22 May 2005  | 9.1  | 0.4                       | 22             |
| 29 May 2005  | 9.5  | 0.6                       | 11             |
| 5 June 2005  | 8.6  | 1.3                       | 11             |
| 12 June 2005 | 7.0  | 0.6                       | 11             |
| 20 June 2005 | 6.8  | 0.3                       | 11             |
| 26 June 2005 | 6.6  | 0.5                       | 11             |
| 5 July 2005  | 6.3  | 0.9                       | 11             |
| 10 July 2005 | 5.5  | 0.4                       | 11             |

#### **Nitrates**

There was no large change in nitrate concentrations over the testing period. The average nitrate concentration of the lake sites remained between 14 and 20 ppm NO<sub>3</sub><sup>-</sup> during the study (see Table 4). The high of 19.15 ppm NO<sub>3</sub><sup>-</sup> was found on 5 July and the low of 14.25 ppm NO<sub>3</sub><sup>-</sup> was measured on 12 June. Each week, the nitrate levels ranged about 3–5 ppm over all lake sites. The creek sites were considerably different, with site 1-B always higher than the average lake level and site 2-B always lower. During the study, site 1-B ranged from 19.74 ppm NO<sub>3</sub><sup>-</sup> (20 June) to 25.51 ppm NO<sub>3</sub><sup>-</sup> (17 July), while site 2-B ranged from 10.55 ppm NO<sub>3</sub><sup>-</sup> (10 July) to 14.70 ppm NO<sub>3</sub><sup>-</sup> (26 June). Since no correction for interference from organic species (which also absorb at 220 nm) was applied, it is possible that these data do not reflect actual nitrate concentrations. The average nitrate concentrations over all weeks of the study were 17.19, 23.33, and 12.62 ppm NO<sub>3</sub><sup>-</sup> for all lake sites, site 1-B, and site 2-B, respectively.

Table 4. Mean nitrate concentration (ppm NO<sub>3</sub><sup>-</sup>) of Brewster Lake sites.

| Date         | Mean  | <b>Standard Deviation</b> | No. of Samples |
|--------------|-------|---------------------------|----------------|
| 22 May 2005  | 17.24 | 2.3                       | 22             |
| 29 May 2005  | 15.52 | 1.0                       | 11             |
| 5 June 2005  | 17.93 | 1.3                       | 11             |
| 12 June 2005 | 14.25 | 0.4                       | 11             |
| 20 June 2005 | 17.45 | 0.7                       | 11             |
| 26 June 2005 | 17.85 | 0.8                       | 11             |
| 5 July 2005  | 19.15 | 0.6                       | 11             |
| 10 July 2005 | 18.05 | 0.7                       | 11             |
| 17 July 2005 | 17.29 | 1.4                       | 11             |

### Hq

The pH of each site did not fluctuate much over the course of the nine weeks (see Table 5). The average pH of the lake (all sites, all weeks) was 8.27. No general trend of increasing or decreasing pH was noted and all sites were very similar. The pH of the creek was a little lower than that of the lake, the average pH of site 1-B was 7.73 and the average pH of site 2-B was 7.79.

The buffer capacity of the lake kept the pH from fluctuating very widely. A healthy pH range for lakes and streams is between 6.5 and 8.5 and most of the measurements fell in

this range. The pH may have been slightly higher when samples were collected during the day because of increased photosynthesis due to sunlight.

Table 5. Mean pH of Brewster Lake sites.

| Date         | Mean | Standard Deviation | No. of Samples |
|--------------|------|--------------------|----------------|
| 22 May 2005  | 8.47 | 0.06               | 22             |
| 29 May 2005  | 8.35 | 0.08               | 11             |
| 5 June 2005  | 8.26 | 0.15               | 11             |
| 12 June 2005 | 8.04 | 0.04               | 11             |
| 20 June 2005 | 8.17 | 0.10               | 11             |
| 26 June 2005 | 8.24 | 0.13               | 11             |
| 5 July 2005  | 8.42 | 0.10               | 11             |
| 10 July 2005 | 8.37 | 0.11               | 11             |
| 17 July 2005 | 8.08 | 0.09               | 11             |

# **Temperature**

The water temperature of the lake generally increased over the course of the study (see Table 6) from a low of 17.9 °C on 22 May to a high of 29.8 °C on 17 July (averaged over all sites measured). The average temperature increased more than 7 °C between 29 May and 5 June, which was the largest increase recorded for consecutive weeks. The average temperature range of the lake sites was 2.14 °C per week. In comparison, site 1-B was usually within 1 °C of the average lake temperature while site 2-B was often several degrees cooler than the lake. In addition, site 1-B was always significantly warmer than 2-B (average difference 9.5 °C, not including the final week) except the last week when both sites had a temperature of 25.0 °C, which was almost 5 °C cooler than the average lake temperature. The average temperature at site 1-B was 27.6 °C and the average temperature at site 2-B was 20.0 °C.

The increase in the temperature of Brewster Lake and Cedar Creek corresponds to the increase in air temperature during this time. Most of the lake sites and site B-1 were in direct sunlight while site B-2 was shaded all day which reflects for the lower temperature at that site.

Table 6. Mean water temperature (° C) of Brewster Lake sites.

| Date         | Mean | <b>Standard Deviation</b> | No. of Samples |
|--------------|------|---------------------------|----------------|
| 22 May 2005  | 17.9 | 0.5                       | 22             |
| 29 May 2005  | 18.4 | 0.9                       | 11             |
| 5 June 2005  | 25.6 | 0.6                       | 11             |
| 12 June 2005 | 28.2 | 0.8                       | 11             |
| 20 June 2005 | 23.6 | 0.6                       | 11             |
| 26 June 2005 | 29.5 | 1.1                       | 11             |
| 5 July 2005  | 28.8 | 0.7                       | 11             |
| 10 July 2005 | 29.1 | 0.5                       | 11             |
| 17 July 2005 | 29.8 | 0.5                       | 11             |

## **Phosphates**

The phosphate levels in the lake were very low according to our results. The average range was 0.1695 mg PO<sub>4</sub><sup>3-</sup>/L for the lake and 0.0603 mg PO<sub>4</sub><sup>3-</sup>/L for the creek. The average concentration of phosphate in the lake over the course of our study was 0.9471 mg PO<sub>4</sub><sup>3-</sup>/L and 0.5037 mg PO<sub>4</sub><sup>3-</sup>/L in the creek. Unfortunately, at the end of the study, the electronic data storage device (USB drive) used to collect the phosphate results was lost and no backup copy was available. We believe that the phosphate concentrations should be higher that those reported here but have been unable to discover any procedural or mathematical error in our results.

#### CONCLUSIONS

Water samples from Brewster Lake were analyzed over nine weeks between mid-May and late-July 2005. The lake water was generally homogeneous with respect to the seven analytes measured but the lake water was considerably different from water taken from two points along Cedar Creek. We were unable to test the effects of precipitation due to a lack of rainfall during the study period. In summary, water temperature increased; dissolved oxygen, alkalinity, and conductivity decreased; nitrate concentration and pH remained constant. The phosphate results were inconclusive.

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### **REFERENCES**

Greenberg, A. E.; Clesceri, L. S.; Eaton, A. D., eds., *Standard Methods for the Examination of Water and Wastewater*, 18<sup>th</sup> ed., American Public Health Association, Washington, D.C., 1992.

United States Environmental Protection Agency, *Volunteer Stream Monitoring: A Methods Manual*, EPA 841-B-97-003, November 1997. {http://www.epa.gov/volunteer/stream/index.html; accessed January 2005.}

