The Effect of Nitrates from Precipitation on the Changing Environment in the Lake Macatawa Watershed

Colleen Iversen
Nathan Whitmyer
Christopher Cappa

GES 401

15 December 1999

I. Introduction and Background

The Lake Macatawa watershed is an area located on the Eastern Shore of Lake Michigan, encompassing Holland and including parts of two counties and several townships (Figure 1).

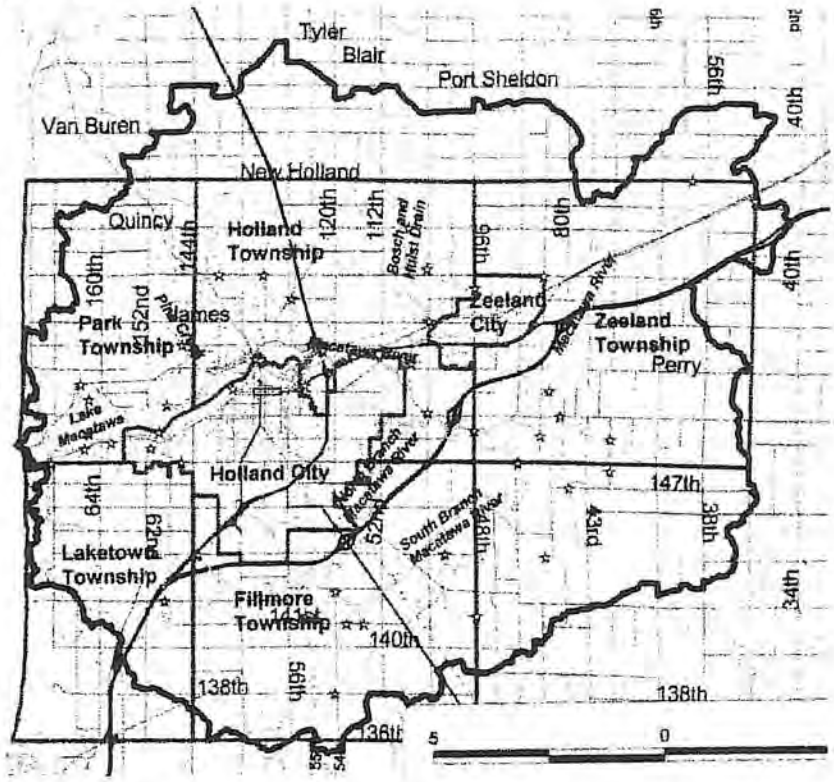

Figure 1. The Lake Macatawa Watershed.

In the past four years, especially in 1999, this watershed has been repeatedly and professionally sampled and studied in order to determine the cause of the hypereutrophic conditions of the lake, or the nutrient over-enrichment found throughout most of the rivers and streams that drain into Lake Macatawa. It was found that many pollutants, in particular phosphorous, contribute to this eutrophic environment (MACC 1999). The water quality of the watershed was found to be low as measured by several factors: amount of phosphorous, temperature, dissolved oxygen, chlorophyll-a, secchi disk depths, and nitrates (MACC, 1999). The Michigan Department of Environmental Quality (MDEQ) was responsible for much of this sampling, and conducted an extensive study of more than forty sites with phosphorous as a pollutant (MACC, 1999).

Due to the abundance and negative influence of these pollutants the goal of the Macatawa Area Coordinating Council (MACC) over the next ten years is to drastically reduce the phosphorous content in the watershed. This task will be accomplished through the education of the public and the implementation of many other best management practices, or suggestions for the reduction of pollutants into the watershed (MACC, 1999).

The Hope College GES 401 class is undertaking several research projects that will seek to improve the environment in the Lake Macatawa watershed. The goal of these research groups is to conduct several studies in which the effectiveness of these best management processes will be determined, or new information about the chemistry, location, and or source of these pollutants will be determined. This research team has chosen to address the pollutant nitrate because nitrate has not been studied as extensively as phosphorous. In particular, we have examined the amount of nitrates in precipitation and the relationship between nitrates in precipitation and nitrate levels in the watershed.

Nitrates enter rainwater by the reaction of nitrogen oxides (NO_x species) with water to produce HNO_3, which dissociates into H^+ and NO_3^- (MARYP, 1999). NO_x species come from some natural sources such as lightning or volcanic gases, however the majority (95%) of nitrates come from anthropogenic sources such as industry and automobiles (MARYP, 1999). It has been suggested that atmospheric deposition may account for a large proportion of nitrate flux into lakes (Manny and Owens, 1983). A study done on nitrates in rainwater in Venezuela showed that greater amounts of nitrates were found in precipitation in areas downwind from urban centers in comparison to more rural areas (Morales *et al.*, 1998). Therefore, we have also investigated the effect of storm direction on nitrate levels in rain because Holland is just northwest of Chicago and storms often come in from this direction. It is thought that precipitation in Holland will therefore show relatively high nitrate concentrations. Figure 2 gives previous measurements on nitrate concentrations in rainwater where relatively high levels are observed regionally (National Atmospheric Deposition Program, 1998).

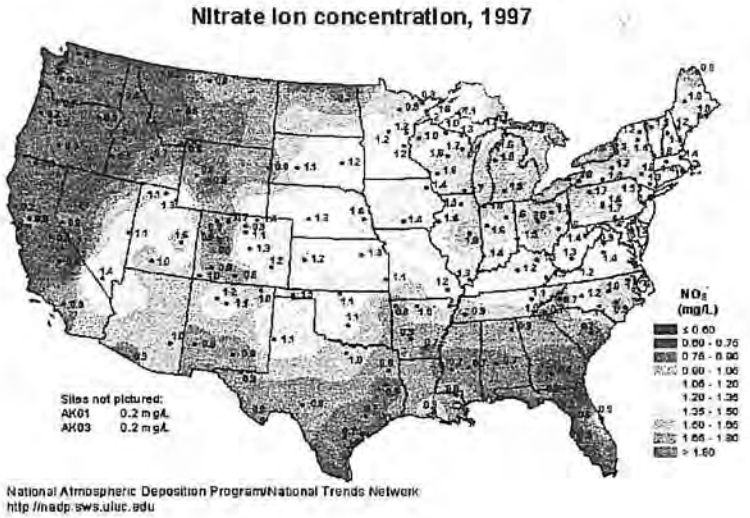

Figure 2. Nitrate concentration in rainwater as measured in weekly samples.

II. Methods

To sample both precipitation and surface water of the Macatawa River two sample sites were chosen on the north branch (N 42°46', W 86°2') and on the main branch (N 42°47', W 86°2') (Figure 3).

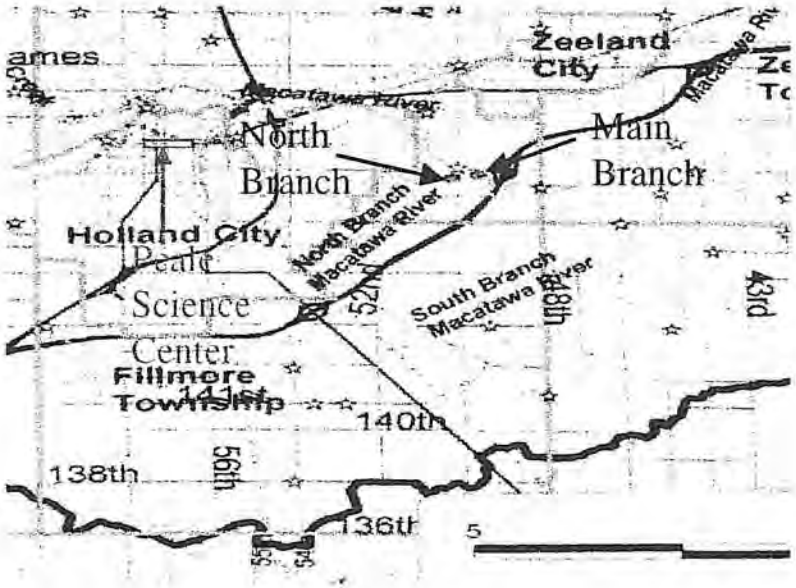

Figure 3. Map indicating the sampling sites for the north branch, main branch and roof of Peale Science Center.

The first site was along the main branch of the Macatawa River at the corner of 16th street and 50th street. The river at this site was approximately 35 ft wide and had a maximum depth of approximately 4 ft. The river at this point moved steadily. The second site was along the north branch of the river. This branch was very narrow, shallow and flowed less swiftly than the main branch.

The standard river water sampling technique involved rinsing a 250 mL Nalgene bottle three times with the river water and then collecting a water sample. Initially, sampling was done three times weekly (Monday, Thursday and Saturday). After two weeks, sampling was done daily. Two samples were collected from each site on each date.

Rainwater catchment devices were used to collect rainwater samples. These were typically composed of a 250 mL Nalgene bottle with a 150 mL powder funnel duct taped to the bottle opening. Three bottles were placed in the ground on the bank of the river by each river sampling site. After every rain event the bottles were collected and replaced. The sampling period was from October 2, 1999 until November 11, 1999. Some of the collected samples contained leaves that had fallen into them. Collected samples were stored in the dark in a refrigerator at 4°C.

The samples were analyzed using ion chromatography (IC). This technique separates ions based on their affinity for the column. The column used was a Dionex model AS11-HC 4-mm (10-32) column. A 30 mM NaOH solution was used as the solvent. The retention time for nitrate was about 5.2 min. The output is given as an area which corresponds to a particular concentration of nitrate. The absolute concentration was determined by making a Beer's law plot using standards over the range 0 ppm to 20 ppm NO_3^-. The samples were diluted in order to make sure that they were within this range.

In addition to the collected rainwater and river samples, tests were done using both pure water and leaf samples. The pure water samples were done by adding distilled water to a Nalgene bottle and allowing this sample to sit in the refrigerator for 3 days. Leaf samples were made by placing a few leaves in a Nalgene with 25 mL water and allowing

them to sit for 3 days. The leaves that were tested included the White Oak (*Quercus alba*), Sugar Maple (*Acer saccharum*), Black Willow (*Salix nigra*), and Goldenrod species (*Solidago*).

A third sampling site was added where leaf contamination was non-existant (the roof of Peale Science Center) in order to determine whether the presence of leaves in the rain samples had a significant contribution to the nitrate concentration.

Using the Hysplit model provided by NOAA, a back trajectory of the path of each storm was determined for the 24 hours prior to its arrival and deposition in Holland. The model was set up assuming a storm height of 500 m in Holland.

III. Results and Discussion

River:

The average nitrate concentration in the main branch of the Macatawa River was 114 ppm. Figure 4 shows the nitrate concentration as a function of date for the main branch.

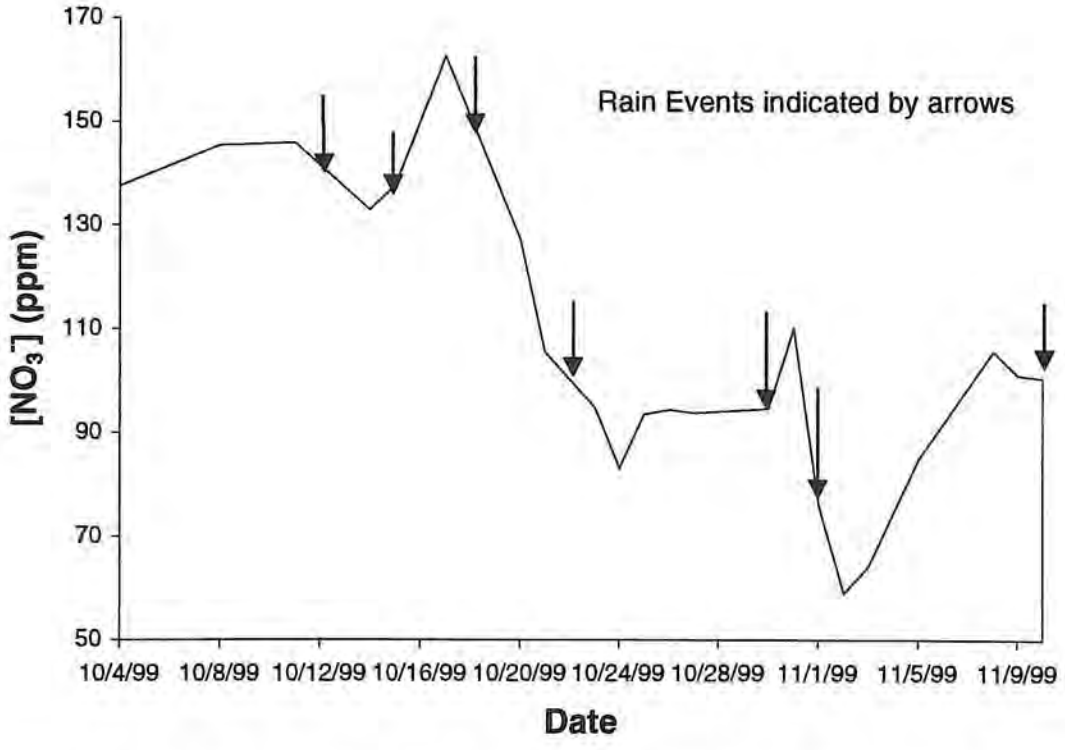

Figure 4. $[NO_3^-]$ in the main branch of the Macatawa River from 10/2/99 to 11/11/99.

The rain events are indicated on the above graph. From this, it can be seen that there is no correlation between rain events and nitrate concentration in the river. Immediately following the rain events on 10/16 and 10/30 the nitrate concentration increased, however after the rain events on 10/13, 10/19, 10/22 and 11/2 the concentration decreases. We suggest that the flux of nitrate in the river is much to complicated to be determined from our study. Complicating factors such as runoff and groundwater contribute nitrates in an indeterminable manner. Estimated background concentrations of nitrate in surface water for streams is less than 0.6 ppm, however this data is for the Grand Teton region. Estimated nitrate concentrations in streams were found to be typically higher in agricultural and urban areas than in undeveloped regions (Mueller et al, 1996). The nitrate concentration in the north branch was determined to be <1 ppm (the detection limit of the IC) and did not increase to a detectable amount after rain events.

Rainwater:

The concentration of nitrate in the rainwater varied between dates, however it was consistent between sites within a date. Figure 5 shows the nitrate concentration at each site for each rain event. The last two sampling dates include data from the roof of Peale Science Center.

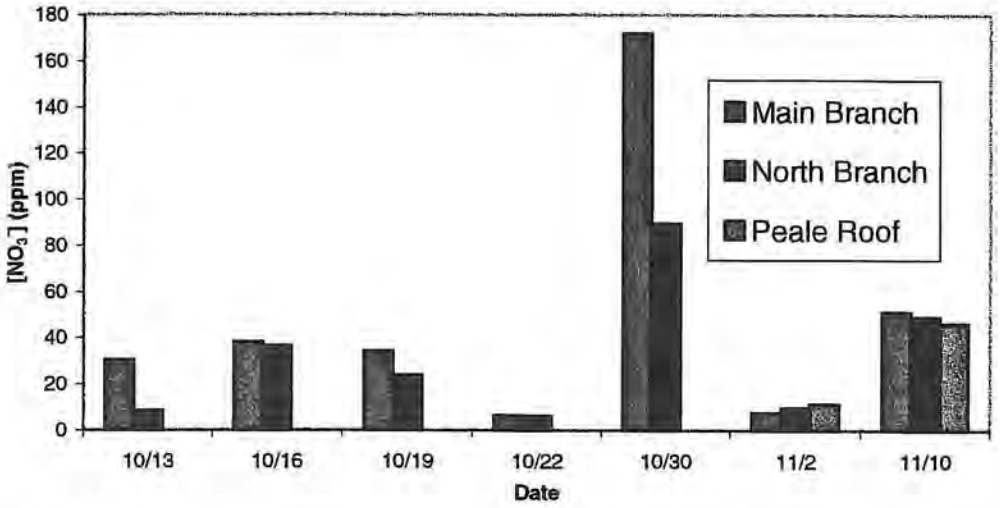

Figure 5. Average $[NO_3^-]$ in precipitation for • the main branch site, • the north branch site, and the • Peale roof site for the sampled dates. Data for the Peale Roof was only collected on 11/2 and 11/10.

Statistical tests could not be performed on the collected data due to the small sample size, however an intra-date comparison of the data indicate it is valid. With the exception of 10/13 and 10/30, the nitrate concentrations between sites are similar. In particular, similarities between sites for the data from November 3 and November 11, which include the roof of Peale, show that contamination at the main branch and north branch sampling sites was minimal.

Additionally, the pure water samples contained undetectable nitrate levels and the leaf samples contained at most small concentrations of nitrate, nowhere near the levels measured in rainwater, again indicating contamination in the rainwater samples was minimal.

The measured nitrate concentrations in our rainwater samples were elevated in comparison to other literature. In a study conducted by the Monitoring Acid Rain Youth

Program (MARYP) in Ontario, nitrate concentrations were found to range from 2 - 11 ppm (1995). On two of our sampling dates the nitrate concentration was within this range, but for the majority of our samples the concentration was found to be higher. Morales *et al.* found that nitrate concentrations in rainwater in a rural area ranged from 0.2 – 3.7 ppm and in a more urban area ranged from 0.2 – 9.2 ppm (1998).

Storm Direction Effects:

Figure 6 shows the back-trajectory for each storm and the average nitrate concentration associated with each precipitation event.

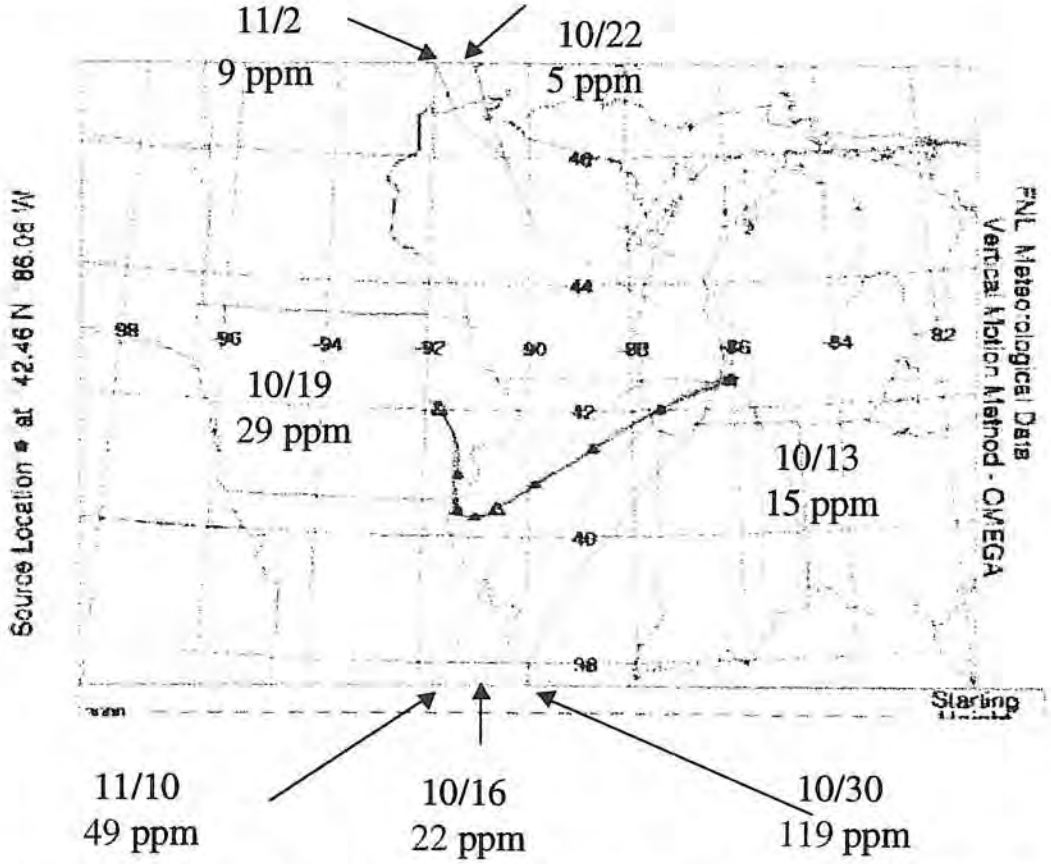

Figure 6. Back-trajectory from Holland, MI of the storm path for each monitored rain event. Storm data was acquired using the HYSPLIT model (NOAA, 1999).

Nitrate concentrations were typically higher in storms that traveled through the Chicagoland area. The highest levels were detected in the storm that traveled directly through the Gary area on 10/30. The minimal concentration from a storm that traveled

through Chicago was 22 ppm. In contrast, the highest average nitrate level from precipitation that did not travel through this area was 15 ppm. We were not able to perform statistical analysis on this data due to the small sample size. These differences are thought to arise due to the heavy industry in Chicago and the smaller amount of such industry in northern Wisconsin and western Michigan. In a study done in Venezuela, it was found that nitrate levels in rainwater near urban sites were elevated in comparison to more rural sites, in accordance with our data (Morales, 1998).

NO_x in the atmosphere:

In order to evaluate whether the detected concentrations of nitrate in rainwater gave reasonable estimates for NO_x concentrations in the atmosphere calculations were done using Henry's Law. Henry's Law is given as $X = p \cdot K_H$, where X is the mole fraction of the solute (which is ~ $[NO_3^-]$ for our system), p is the partial pressure of the gas, and K_H is the Henry's Law coefficient. The Henry's Law coefficient for NO_2 at 298 K is 0.012 (mol/kg)/bar while for NO K_H = 0.0019 (mol/kg)/bar. Therefore we used the value for NO_2. Assuming $[NO_3^-]$ = 30 ppm we calculate a partial pressure of 0.042 bar NO_2. This is 4.1% of the total atmospheric pressure, which is quite high, even for polluted regions. However, K_H increases as temperature decreases and temperature decreases with altitude. Therefore, a lower partial pressure for NO_2 would be necessary at the altitude where NO_2 would dissolve into rainwater.

IV. Future Studies

1. A continuation of the above study, however looking at the effect of season on the relationship between rainwater and river water. A USGS study has shown that there is a seasonal effect in that during the summer months nitrate concentrations are higher relative to the other seasons. This difference is thought to be due to elevated agricultural land use during the summer months.
2. A more detailed study of the effect of storm direction on nitrate concentration in rainwater. This would necessitate a joint effort with schools in Chicago and further to the west of Chicago.

3. To analyze the pH of the rainwater in connection with the concentration of nitrate.

V. Conclusions

There was no correlation found between precipitation events and nitrate levels in the river water of the Macatawa River. The nitrate concentrations in the main branch of the Macatawa river were on average 114 ppm while in the north branch the concentration is less than 1 ppm. The concentration of nitrate in rainwater varied between dates but was consistent between sampling sites on a given date. Typically, higher nitrate levels were found in precipitation events from storms that traveled through the Chicagoland area as compared to those that came from northern Wisconsin.

Despite the high nitrate concentrations in the rainwater, it is thought that rainwater contributes minimally to nitrate levels in the Macatawa River. We contend that other sources of nitrate, such as runoff or groundwater, complicate our analysis making it difficult to estimate an exact contribution.

VI. References

MACC. "The Macatawa Watershed Project". On-Line: www.macatawa.org/~macc, 19 September 1999.

Manny, B. A., Owens, R. W. 1983. Additions of nutrients and major ions by the atmosphere and tributaries to nearshore waters of northwestern Lake Huron. *Journal of Great Lakes Research*. 9: 403-420.

Monitoring Acid Rain Youth Program (MARYP). "Nitrate, Chloride, Phosphate, Calcium." On Line: http://www.trentu.ca/academic/biology/maryp/1996finalreport/rain2b.html, 3 October 1999.

Monitoring Acid Rain Youth Program (MARYP). "Rainfall Chemistry." On-Line: http://www.trentu.ca/academic/biology/maryp/1996finalreport/rain.html, 3 October 1999.

Morales, J.A., Bifano, C., Escalona, A. 1998. Atmospheric deposition of SO_4-S and (NH_4 + NO_3)-N at two rural sites in the western Maracaibo Lake Basin. *Atmospheric Environment.* 32(17): 3051-3058.

Mueller, D. K., Helsel, D. R. 1996. Nutrients in the Nation's Waters: Too Much of a Good Thing? *U.S. Geological Survey Circular 1136.*

National Atmospheric Deposition Program (NRSP-3)/National Trends Network. (1998). NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820. On-Line: http://hadp.sws.uiuc.edu, 19 September, 1999.

National Oceanic and Atmospheric Association (NOAA). On-Line: http://www.arl.noaa.gov/ready/hysplit4.html, 21 November 1999.