Nutrient Geochemistry in North Central Ohio Lakes

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By

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Abstract

Eight lakes in north central Ohio have been sampled to review their nutrient chemistry. Analysis was also done to compare the variation in nutrient concentration at primary locations of recharge and discharge. Five of the lakes have primary inlet and outlet stations which have also been sampled. The three reservoirs only have lake sampling measurements. The samples were collected starting in December of 2010 and continued through September of 2012. The lakes would be classified as small and the largest of them is 1350 acres. All of the water samples collected were run through a Skalar nutrient analyzer and tested for $\mathbf{PO_4^{3-}}$, $\mathbf{NH_4^-}$, and $\mathbf{NO_3^-+NO_2^-}$. Once the data was compiled, graphs showed all eight lakes/reservoirs with the variations in chemistry of the three nutrients. Based on the average nutrient concentrations of the lakes studied, they are considered to be in poor biological condition. The data also shows that the lakes are acting as a sink for nitrogen based on the variation of inlet and outlet concentrations. Cyanobacteria decomposition was an important factor in the concentration of ammonium concentrations at various locations sampled in the lakes.

Acknowledgements

I would like to thank all the faculty and staff in the School of Earth Sciences at The Ohio State University. I would particularly like to say thank you to Dr. Ozeas Costa for all of his help through not only this project, but also my Shell Undergraduate Research Experience. His guidance has truly helped me succeed in producing a great poster as well as a great Senior Thesis. Shell's funding in the project helped train me on the topic of water quality. I would also like to thank Sue Welch for her expertise with the Skalar nutrient analyzer. She helped me to troubleshoot whenever issues came about while running the samples. Mary Scott was also very helpful throughout this project in guiding me to find resources. I would like to also thank Dr. Jeff Daniels for all of his expertise in geophysics as well as opening my eyes to many job opportunities in the oil and gas industry. Finally I would like to thank Dr. Anne Carey for her guidance through my undergrad career in Earth Sciences.

Introduction

Nutrient-related pollution significantly impacts drinking water supplies, aquatic life, and recreational water quality. The natural sources of nutrients in the environment are precipitation, soil erosion, and decaying vegetation. The rate of nitrate violations in water systems across the United States has more than doubled in the last decade. (Wagner and Gibson, 2011) Land use plays a critical role on water quality. Agriculture is the leading contributor of nutrients in the Mississippi-Atchafalaya River Basin. Crop production accounts for more than half of the nitrogen and phosphorus that flows into the Gulf of Mexico. (Wagner and Gibson, 2011) Eutrophication is the response to an increase of the natural amount of nutrients in aquatic systems above healthy levels. In aquatic ecosystems, eutrophication leads to a wide range of ecological problems, including toxic algal blooms, loss of oxygen, fish kills, disruption of food webs, and loss of biodiversity (including species important to commercial and sport fisheries and shellfish industries). Human health problems have also been associated with nutrient pollution. (Camargo and Alonso, 2006) Some of the algal species that take advantage of the excess in nutrients produce powerful toxins that can harm humans and animals. (Todd, 2006) The two primary nutrients that correlate with increased algal abundance are nitrogen and phosphorus.

Compared to streams and rivers, lakes have a much longer water residence time which will reduce the amount of nutrient export. The first National Lakes Assessment (NLA) conducted by the EPA in 2007 found that over 22% of US lakes and reservoirs above 10 acres are poor in biological condition.(U.S. EPA, 2012) Poor habitat conditions along the lakeshore and high levels of nutrients are the most significant stressors of those assessed in the survey. They found that the nutrients nitrogen and phosphorus are at high levels in about twenty percent of lakes, and that poor biological health is 2.5 times more likely in lakes with high nutrient levels.

For this study, eight lakes and reservoirs located in north central Ohio have been sampled. These lakes/reservoirs vary in size from 28 to 1350 acres. The watershed catchments for these lakes/reservoirs vary in land use from parks to cropland, to urban developed landscapes. This variation in land use will be reviewed to compare its effects on the watershed chemistry. Among the studied aquatic systems, the three smaller reservoirs used for water supply receive no recharge from any river or stream. Primary recharge in these reservoirs comes from precipitation.

The overall goal of this research is to evaluate the nutrient geochemistry of eight lakes/reservoirs in north central Ohio. Variations in **PO_4^{3-}** , **NH_4^-** , and **$NO_3^-+NO_2^-$** water concentrations were the primary area of study. Comparisons of the differences between each of the eight systems were made. Multiple sites were sampled in each of the systems, allowing for a comparison of nutrient concentrations between inlet and outlet stations. Such information is used to determine the role of these systems as sink or sources of nutrients to the watershed, as well as the rate of nutrient discharge. Variations in the concentrations throughout the year were also calculated to see changes in the lake chemistry over time.

Literature Review

Land Use

A study at Lake Calumet in Chicago was done trying to estimate runoff and nonpoint source pollutant concentrations around Lake Calumet. The study employed ArcHydro GIS to create a model which accounted for nine different variables.(Wilson and Weng, 2010) from their calculations they found that the residential catchments increased the Total Nitrogen concentration by 1.82mg/l. The agricultural catchments were the highest at 4.51mg/l and the forested catchment had a Total Nitrogen concentration of .7mg/l. The phosphorus concentrations had a similar pattern with the residential, forested and agricultural concentrations at .83mg/l, .01mg.l, and 1.3mg/l respectively. (Wilson and Weng, 2010) The conclusions of the study stated that an increase in runoff contributed to a differential increase in concentration of almost every single pollutant studied. The study also concluded that an increase in urban land development over a nine year period had a direct correlation with an increase in pollutant concentrations within the watershed.

Nutrient Removal

A global study of lakes was done in order to figure out the amount of nitrogen removal that occurs within lakes. Although lakes and reservoirs only occupy 6% of the global lentic surface area, it is estimated that they retain almost 33% of the total nitrogen removed by lentic systems. (Harrison et al, 2009) Once the nitrogen has entered surface waters it has multiple potential fates, including permanent loss via denitrification, sediment burial, and temporal storage in biomass.(Saunders and Kalff, 2001) Using mathematical modeling, the study's results showed that aquatic systems larger than .001 square kilometers removed about one third of the nitrogen that entered the surface waters. The model also estimates the lentic systems removal rate of 4,805 kg N per kilometer squared per year globally.(Harrison et al, 2009) The model also indicates that small lakes remove more than twice as much nitrogen from watersheds as large lakes. Because this was a global study, the spatial heterogeneity of lakes has many different factors that affect the nitrogen removal rate. Some lakes have the ability to removal almost all of the surface nitrogen added into them while others may removal only a very small percentage.(Harrison et al, 2009)

Water Quality Classifications

The National Lakes Assessment (NLA), undertaken by the U.S. EPA in 2007, is the first statistical survey of the condition of our nation's lakes, ponds, and reservoirs. Based on the sampling of over 1,000 lakes across the country, the survey results represent the state of nearly 50,000 natural and man-made lakes that are greater than 10 acres in area and over one meter deep.

Field Site Description

The eight lakes sampled for this research are located in north central Ohio in the Mohican River watershed. (Figure 1)

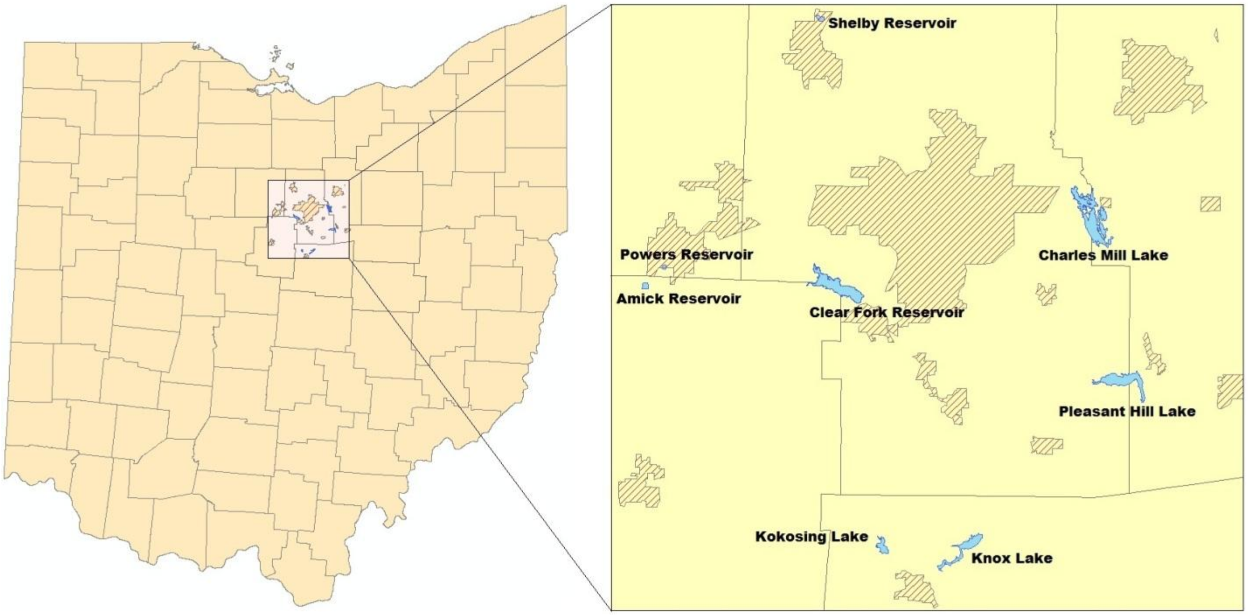

Figure 1: General Reference Map with the location of all eight lakes/reservoirs.

For the larger lakes, samples were taken at the primary inlet, at a representative station within the lake, and at the outlet. Some lakes had more than three sampling sites due to their unique physical settings. For example, besides its inlet and outlet sampling stations, Charles Mill Lake also had two sampling sites within the lake, each designed to sample water exchanges between each of its major sections (Figure 2).

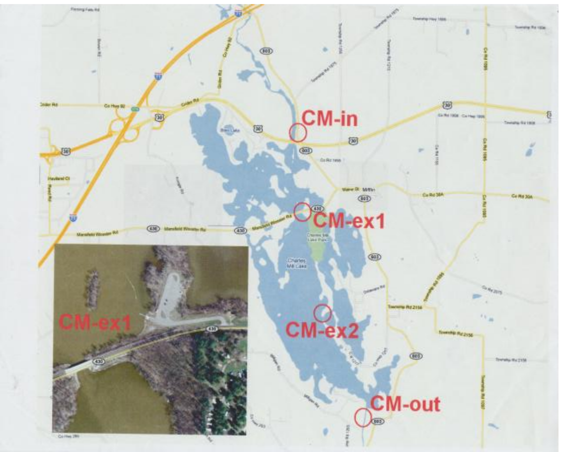

Figure 2: Charles Mill Lake Sampling Locations

Clear Fork Reservoir only had one lake station, but two inlet stations (Figure 3), each sampling one of the primary inflows into the reservoir.

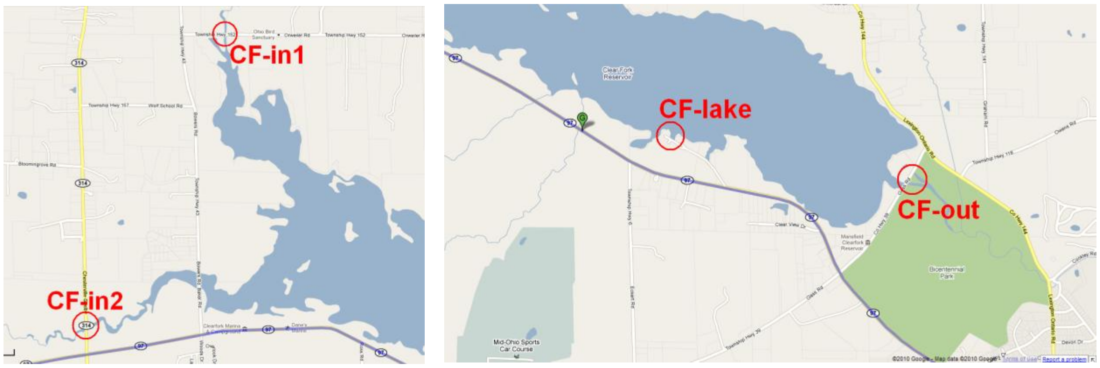

Figure 3: Clear Fork Reservoir Sampling Locations

Since the three smaller reservoirs (Amick, Powers, and Shelby reservoirs) did not have any inlet or outlet stations, they only had a lake station (Figure 4). These smaller reservoirs are used as water supply for the cities of Galion (population 10,416 – July 2011) and Shelby (population 9,242 – July 2011).

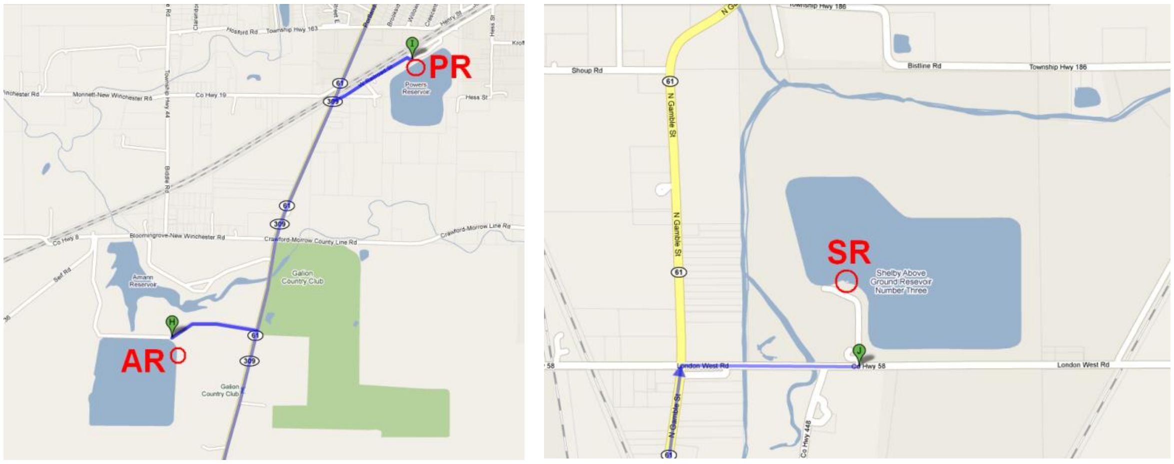

Figure 4: Sampling Locations for Amick, Powers, and Shelby reservoirs

Methods

Water samples have been collected from Charles Mill Lake, Pleasant Hill Lake, Knox Lake, Kokosing Lake, Clear Fork Reservoir, Amick Reservoir, Powers Reservoir and Shelby Reservoir. The samples have been collected monthly between December 2010 and September 2012. There was also one rainfall collector at a central location in the region. Samples of rainwater and snow were analyzed to provide a measure of the nutrient input from atmospheric precipitation. Samples were filtered immediately after collection (through Whatman GF/C glass microfiber filters) using a Nalgene filtration unit connected to a hand pump. Samples were kept in the dark in a cooler and frozen no more than 6 hours after sampling. They were kept frozen until analysis. In addition, water and air temperature, pH, and concentration of total dissolved solids were also measured in situ using portable meters (Fisher Scientific accumet AP72 and AP75).

A Skalar SAN++ nutrient analyzer was used to determine the concentrations of each sample. The analyzer runs one water sample at a time which takes about three minutes. Two different analytes can be tested at one time. The machine works by sending the sample through a series of mixing coils. An indicator is mixed into the sample which changes the color of that sample in accordance with the concentration of the analyte. Once the sample is mixed and its color change, it flows into the detector which determines the intensity of the color and, by association, of the analyte concentration. Solutions for the phosphate and ammonia calibrations were made using standards with 0, 50, 100, 200, 500, and 1000 parts per billion. The calibration for the nitrate+nitrite solutions were made with 0, 100, 200, 500, 1000, and 2000 parts per billion. When a sample had a concentration that was higher than the highest calibration concentration, a dilution was performed on the sample. For example, if one milliliter of the sample was pipetted into a test tube and five milliliters of deionized water were added, the new solution concentration would be multiplied by six. A tracer with a high concentration (500 ppb) of the nutrient was run every ten samples. This was done in order to ensure that any drift in the baseline would be accounted for in the analysis. That tracer was followed by a wash to ensure that it does not contaminate the other samples that are being run.

Results

Average PO43- concentrations in Charles Mill Lake (0.129 mg/L) was about twice the maximum values observed at lakes in the same nutrient ecoregion (Cornbelt Plains – as described in Omernik, 1995)). All other lakes/reservoirs studied had PO43- concentrations lower than 0.050 mg/L. The smallest reservoirs had the lowest PO43- concentrations: Amick Reservoir = 0.020 mg/L; Powers Reservoir = 0.014 mg/L; Shelby Reservoir = 0.012 mg/L. The lowest average PO43- concentration among the larger lakes/reservoirs was observed at Pleasant Hill Lake (0.032 mg/L). Standard deviation values between samples were also much higher in the high-concentration cohort (Fig. 5A).

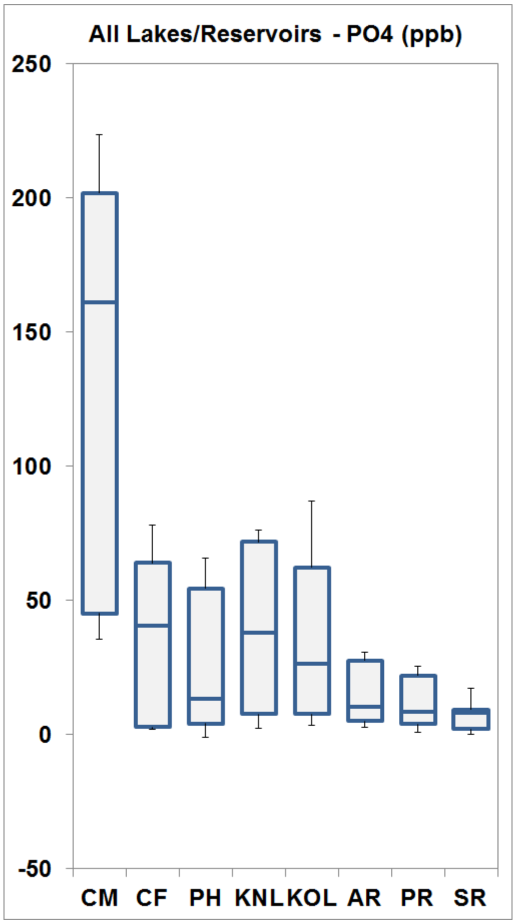

Figure 5A: Boxplots showing PO_4^{3-} concentration in all studied lakes/reservoirs. Lines in the middle of bars indicate median values (middle of dataset); the top of bars indicate upper quartile – 25% of data greater than this value – and the bottom of bars indicate lower quartile – 25% of data less than this value). Whiskers indicate maximum and minimum values (excluding outliers).

Average NH_4^- concentration in Charles Mill (0.143 mg/L) was about 2 times higher than the averages for all other lakes/reservoirs (Fig. 5B). With the exception of Knox Lake (0.115 mg/L), average NH_4^- concentrations for all other large lakes/reservoirs were lower than 0.080 mg/L. Unlike the observed for PO_4^{3-}, concentrations of NH_4^- at the smaller reservoirs were among the highest (Amick Reservoir = 0.083 mg/L; Powers Reservoir = 0.067 mg/L; Shelby Reservoir = 0.083 mg/L).

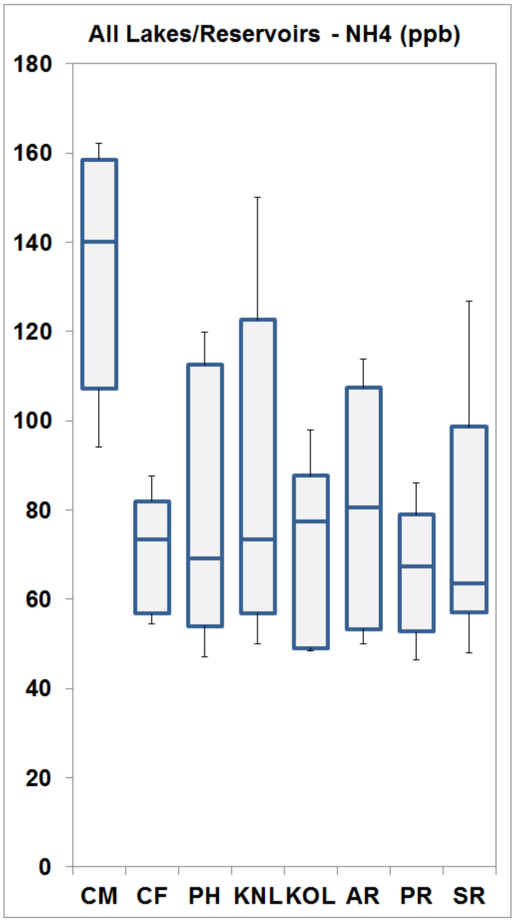

Figure 5B: Boxplots showing NH_4^- concentration in all studied lakes/reservoirs.

Average TON concentration in Charles Mill Lake (0.325 mg/L) was the lowest among all studied lakes/reservoirs, except for Powers Reservoir (0.298 mg/L). Seasonal variability is an important factor controlling these differences in TON data between Charles Mill and the other studied sites. Charles Mill was the only site in which standard deviation of TON concentrations were lower than the average. The lakes/reservoirs with the highest seasonal variability were Kokosing Lake (stdev = 0.794 mg/L) and Clear Fork Reservoir (stdev = 0.732 mg/L), where the two highest average TON concentrations were also observed (Fig. 5B). Although dissolved oxygen (DO) concentrations were not measured in the studied lakes, the low concentrations of TON relative to NH_4^- in Charles Mill suggests that anoxic conditions are dominant (low nitrification rates – the conversion of NH_4^- to NO_3^-), which also explain the widespread fish kills observed in this lake.

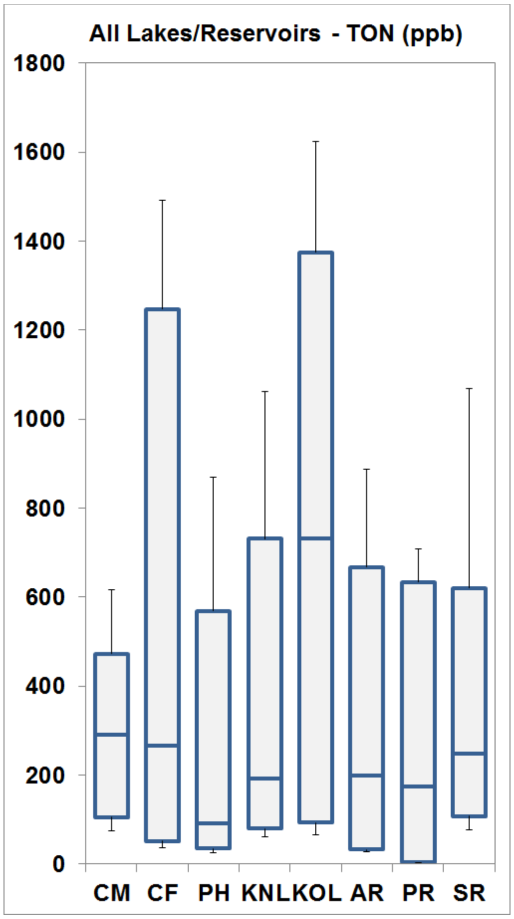

Figure 5C: Boxplots showing TON (total oxidized nitrogen = NO_3^- + NO_2^-) concentrations in all studied lakes/reservoirs.

Differences within lakes: Inlet vs. Outlet Nutrient Concentrations

Sampling was also undertaken at inlet and outlet stations in each of the studied lakes/reservoirs, except for the three smaller reservoirs (Amick, Powers and Shelby). The graphs discussed below are intended to show the three nutrient concentration levels at the primary inlet and outlets of each of the five larger lakes. The reservoirs were not included in this data because the primary source of recharge to the three reservoirs comes from precipitation. These graphs will help to determine how each of the lakes reacts to nutrient runoff.

In general, concentrations of TON and PO_4^{3-} were higher in the inlet than at the outlet (Fig. 6A and 6B). For NH_4^-, the outlet concentrations were higher than the inlet (Fig. 6C).

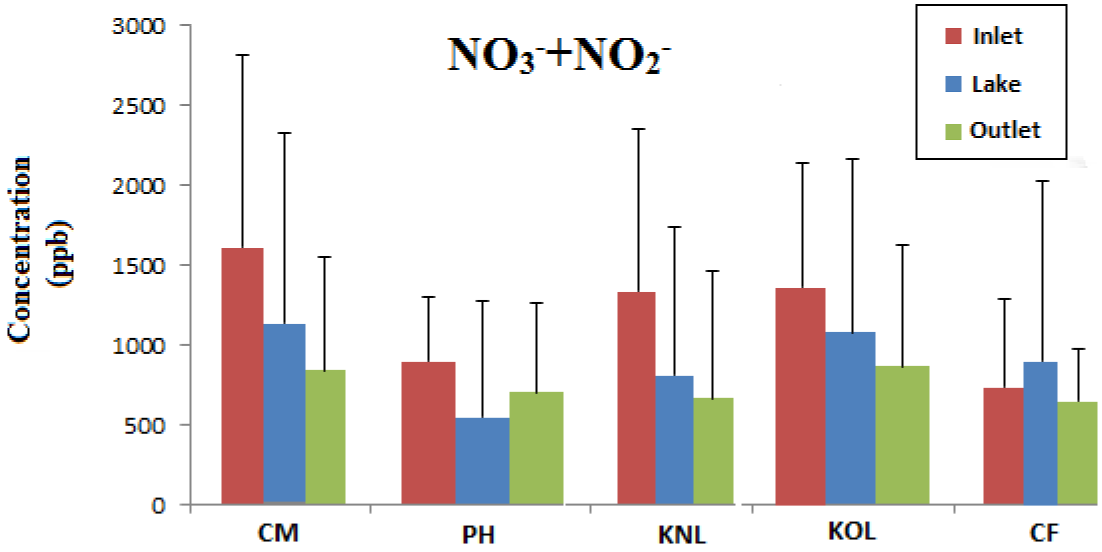

Figure 6A: TON concentrations at the Inlet, Lake, and Outlet Stations.
(CM = Charles Mill Lake, PH = Pleasant Hill Lake, KNL = Knox Lake, KOL = Kokosing Lake,
and CF = Clear Fork Reservoir)

In all the lakes except Clear Fork, the average TON concentrations were the highest at the inlet stations. For all the lakes except Pleasant Hill, the outlet concentrations were the lowest. For all of the lakes the inlet concentrations were higher than the outlet concentrations (53% higher in Charles Mill, 33% in Pleasant Hill, 100% in Knox, 63% in Kokosing, and 14% higher in Clear Fork). In all of the lakes except Clear Fork, the TON concentrations at the inlet were higher than then concentration in the lake (Fig. 6A). At all of the lakes studied the outlet stations had the lowest degree of variation in their standard deviations.

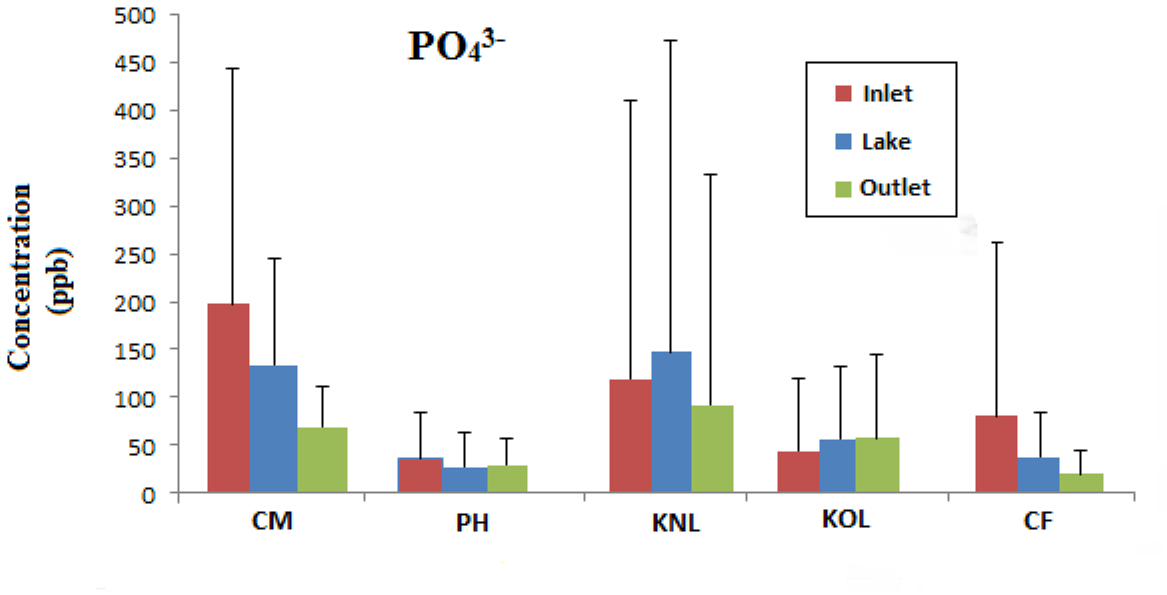

Figure 6B: PO_4^{3-} concentrations at the Inlet, Lake, and Outlet Stations.

In all the lakes except Knox and Kokosing, the average PO_4^{3-} concentrations were the highest at the inlet stations. For all the lakes except Pleasant Hill and Kokosing, the outlet concentrations were the lowest. For all of the lakes except Kokosing, the inlet concentrations were higher than the outlet concentrations (99% higher in Charles Mill, 8% in Pleasant Hill, 35% in Knox and 192% higher in Clear Fork; at Kokosing, the inlet PO_4^{3-} concentration was 39% lower than the outlet). In all of the lakes accept Knox and Kokosing, the PO_4^{3-} concentrations at the inlet were higher than the concentrations at the lake stations. At all of the lakes except Kokosing the outlet stations had the lowest degree of variation in their standard deviations. In all the lakes accept Knox the inlet stations had the highest degree of variation in their standard deviation.

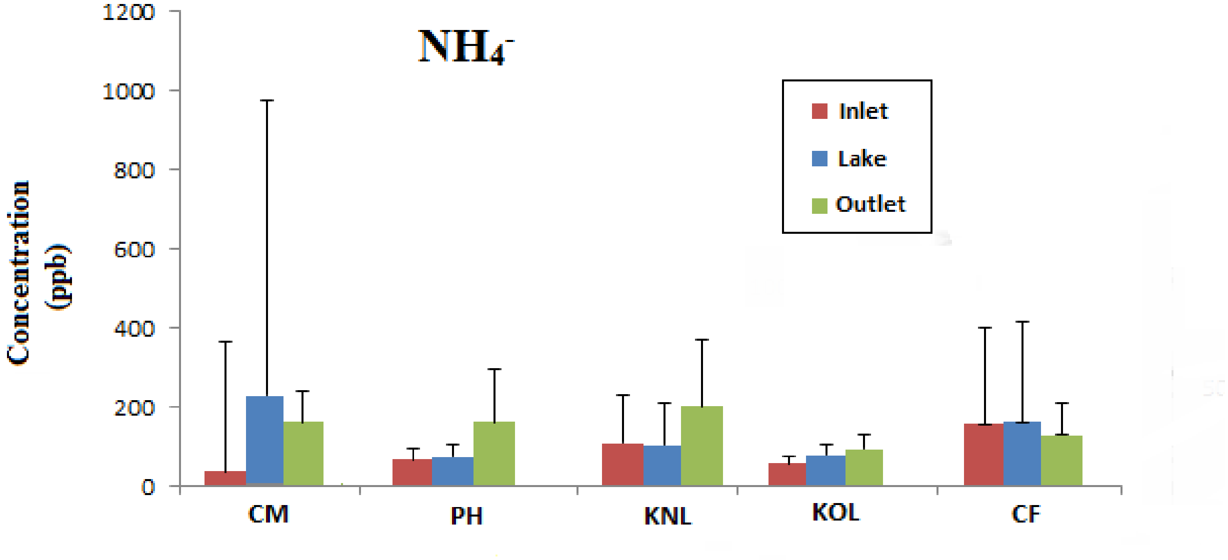

Figure 6C: NH_4^- concentrations at the Inlet, Lake, and Outlet Stations.

In all the lakes except Charles Mill and Clear Fork, the average NH_4^- concentrations were the highest at the outlet stations. For all the lakes except Knox and Clear Fork, the inlet concentrations were the lowest. For all of the lakes except Clear Fork the inlet concentrations were lower than the outlet concentrations (86% lower in Charles Mill, 57% in Pleasant Hill, 39% in Knox and 28% lower at Kokosing; at Clear Fork, the inlet NH_4^- concentration was 10% higher than the outlet). In all of the lakes except Knox, the NH_4^- concentrations at the inlet were lower than the concentrations in the lake stations.

Physical controls: The effects of precipitation (differences between lakes)

Although rainfall has a significant effect on the nutrient concentrations of the studied lakes, the magnitude of such effect differs significantly between lakes and also within sampling stations (inlet, lake and outlet). Cumulative precipitation values for the 5 days preceding sampling were calculated monthly using data from the meteorological station at the Mansfield Lahm Regional Airport (a central location in the study area). The largest effect of rainfall was observed in PO_4^{3-} concentrations (Table 1), with an average of over 200% increase when cumulative precipitation on the 5 days before sampling exceeded 0.6 inch (which is the equivalent to ¼ of the average monthly precipitation in the study area). The precipitation effect also caused an average increase of 94% in NH_4^- concentrations (although Charles Mill Lake and Amick Reservoir experienced decreases – Table 1) and an average increase of about 3% in TON concentrations (with Charles Mill, Amick and Kokosing experiencing decreased concentrations).

Study site	**PO_4^{3-} variation**	**NH_4^- variation**	**TON variation**
Charles Mill	+282%	-80%	-3%
Pleasant Hill	+386%	+320%	+10%
Knox Lake	+403%	+54%	+13%
Kokosing Lake	+250%	+248%	-20%
Clear Fork	+74%	+50%	+16%
Amick Reservoir	+0.5%	-74%	-31%
Powers Reservoir	+147%	+137%	+37%

The increased flux of PO_4^{3-} in periods of increased rainfall significantly altered the N:P ratio of four of the studied lakes/reservoirs, the only exception being the three smaller reservoirs (Amick, Powers, Shelby) and the Charles Mill Lake (Fig. 7). In dry conditions, all the studied lakes/reservoirs experience P limitation (N:P ratio > 35). After significant rainfall, increased supply of P lead to N limitation in Clear Fork, Pleasant Hill, Knox, and Kokosing lakes (Fig. 7).

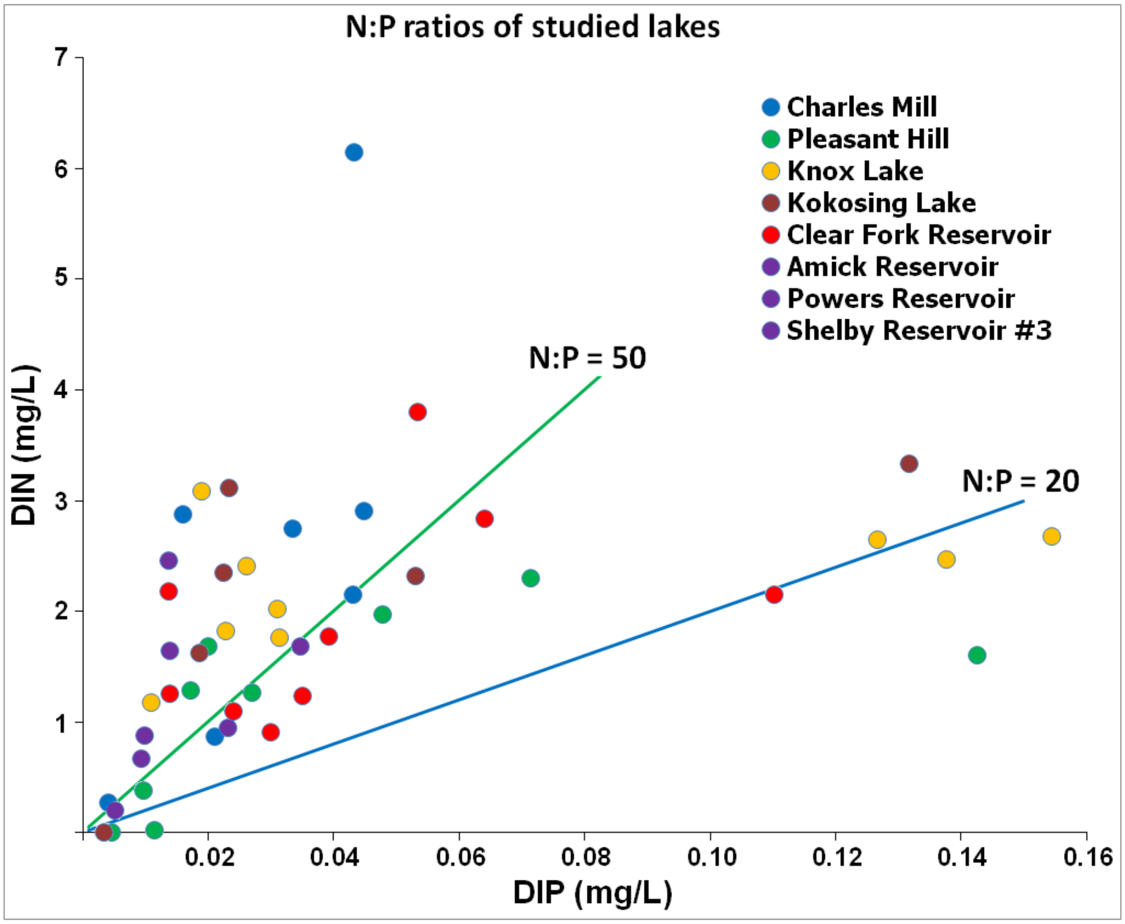

Figure 7: Plots of DIN (dissolved inorganic nitrogen) versus DIP (dissolved inorganic phosphorus) for the studied lakes/reservoirs. Solid lines denote N:P ratios of 20 and 50 which are the ratios below and above which N and P limitation are expected to occur respectively (Guildford and Hecky 2000)

Discussion

In all of the lakes surveyed, the TON concentrations were the highest. The highest yearly average concentration of TON was in Kokosing Lake and the lowest concentration was in Powers Reservoir. The lakes had a higher degree of variation in their standard deviation than the reservoirs. This may be attributed to that fact that the lakes have inlets where a high concentration of TON may flow into them. This can also vary with the amount of precipitation that occurs. The inlet concentrations in all of the lakes had the highest concentration of TON while the outlets had the lowest. This concept refers back to the global study done of lakes and shows that these small lakes are acting as a sink for nitrogen.

PO_4^{3-} had the lowest concentrations of all three nutrients being studied. Typical PO_4^{3-} concentrations in US lakes vary from 0.005-0.050 mg/L (USEPA, 2009). Average PO_4^{3-} concentrations at the three smaller reservoirs all fell in the lower 20% of this range . Most of the larger lakes/reservoirs have average PO_4^{3-} concentrations at the upper 75th percentile of this range. The only exception is Charles Mill Lake, whose concentrations are about 3-fold those found in the other large lakes in this study, Based on their average concentrations, these lakes are considered to be in poor biological condition, according to the parameters defined in the U.S. EPA National Lakes Assessment (USEPA, 2009). In all but one of the lakes studied, the inlet concentration of phosphorus was higher than the outlet concentrations.

The NH_4^- concentrations were the second highest ranging from .144 mg/l to .067 mg/l. The NH_4^- concentrations where different then the two other nutrients studied. In this case, the concentrations were higher at the outlet stations than that were at the inlet. The lake concentrations were also higher than the inlet concentrations suggesting that cyanobacteria decomposition was occurring within the lakes. The byproduct of decomposition by bacteria is NH_4^- which would suggest a large amount of bacterial decomposition is taking place within the lakes. Low NH_4^- values at the inlet suggest that there is minimal bacterial decomposition.

Future Work

There is much more analysis that can be done with the collected data. Correlations between land use and nutrient chemistry can be made to identify what specific types have the largest effect on each individual lake. The precipitation data can also be used to make correlations to the nutrient concentrations. The nitrogen to phosphorus ratio can be compared to identify which lakes have ideal conditions for algal growth. The pH data that was collected can be used to see how the process of denitrification affects lake pH. More statistical analysis comparing the seasonality effects on nutrient chemistry can be looked at to see what times of the year the lake receives the most nutrient inputs. The water temperature data collected can also be used to make correlations to the variation in nutrient concentrations. Testing the samples for cyanobacteria cell count may also be helpful in comparing the nutrient concentrations to them.

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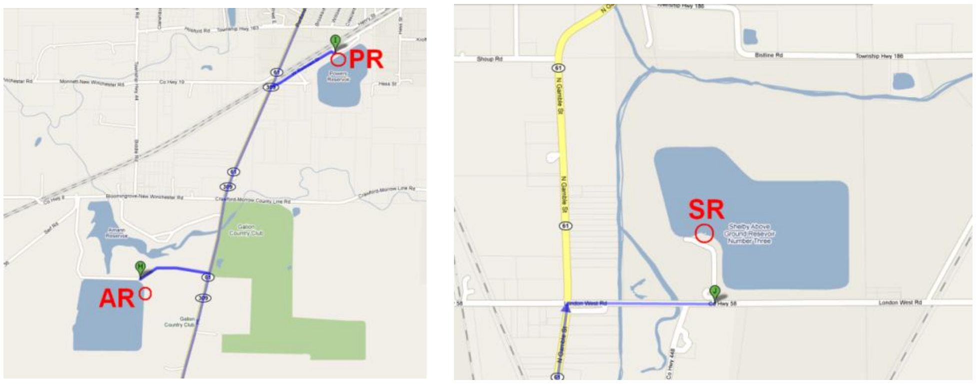
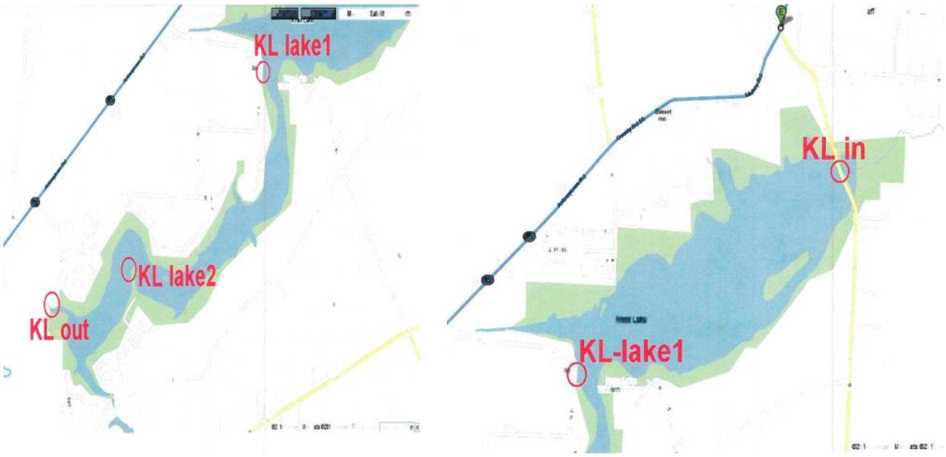
Appendices

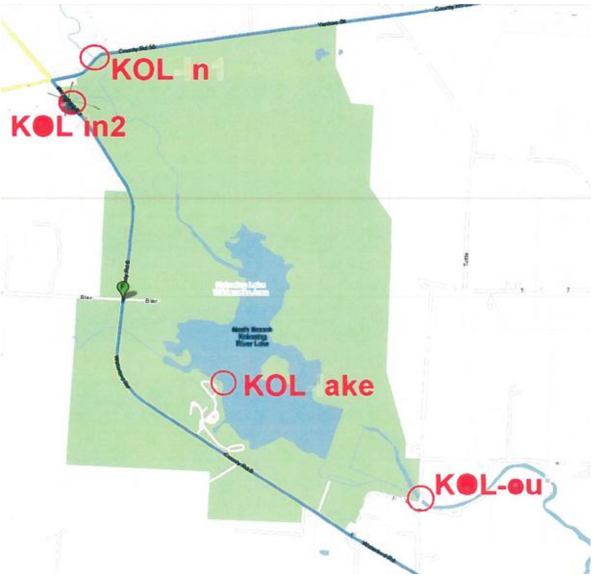
Maps showing the inlet, lake, and outlet stations for Pleasant Hill



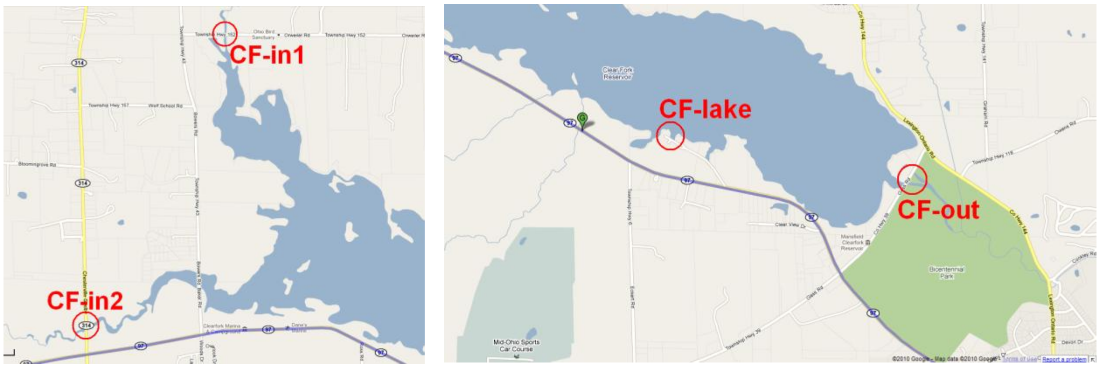
Maps showing lake stations for Amick, Powers, and Shelby Reservoir



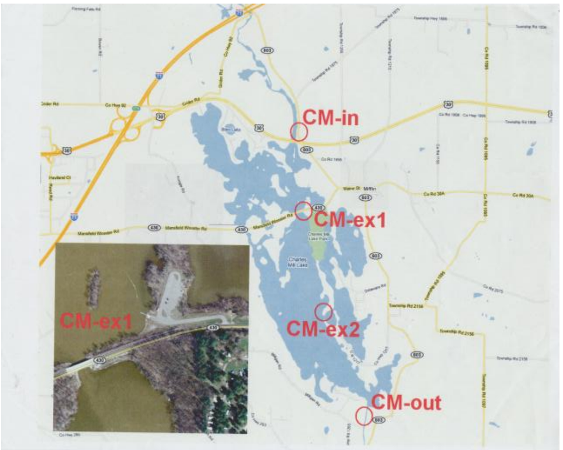
Maps showing inlet, lake 1, lake 2, and outlet stations for Knox Lake



Map showing inlet 1, inlet 2, lake, and outlet stations for Kokosing Lake



Maps showing inlet 1, inlet 2, lake, and outlet stations for Clear Fork Lake



Maps showing inlet, lake 1, lake 2, and outlet stations for Charles Mill Lake