

Analysis of Phosphate Flux in Response to Snowmelt and Rain Events in the Macatawa Watershed

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GES 401

Introduction

The overabundance of phosphorus is a well-documented problem in the Macatawa watershed area. The phosphorus enters the watershed in agricultural regions through runoff of

animal wastes and fertilizers. The effects of rainfall on phosphorus levels in the Macatawa watershed has been studied in the past. The figure below shows the average yearly phosphate concentrations in Lake Macatawa and the surrounding tributaries related to the annual precipitation from 1997 to 2005.

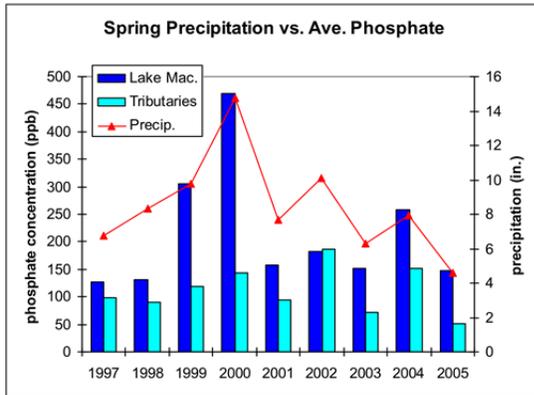


Figure 1. Annual average phosphate concentrations and precipitation from 1997 - 2005

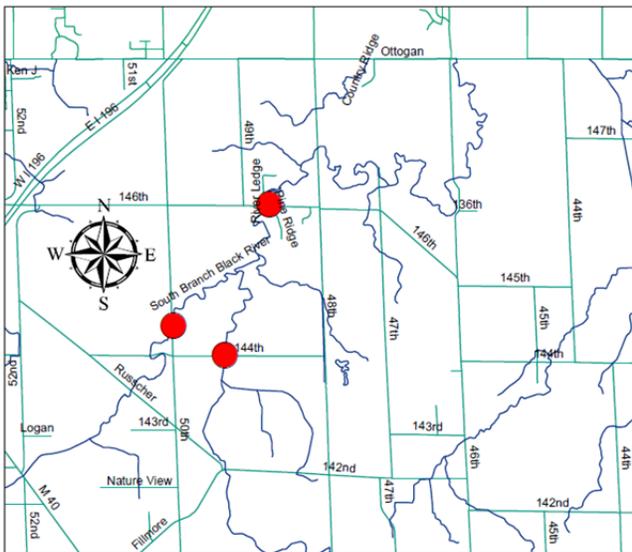
These data demonstrate that the concentration of phosphorus correlates with the amount of precipitation. The annual phosphate concentrations over the eight year range fluctuated between 100 ppb - 500 ppb. The years with a relatively low concentration phosphorus were still much greater than the level that is considered healthy for a lake (25 - 50 ppb). Overall, years that experienced large amounts of precipitation consequently had high levels of phosphorus runoff.

The effect of snow on phosphorus in the Macatawa has not been as closely studied; however, phosphorus runoff due to snowmelt has been extensively studied in northern regions, such as Canada, where snowmelt is the dominant force that affects phosphorus runoff. These studies found various factors that influenced the amount of phosphate runoff. One factor was soil temperature. In winter and early spring the ground is still frozen, so there is little soil erosion and phosphate flux. As the ground warms, the top layer thaws and is more easily eroded, causing an increase in the amount of soil loss and attached phosphorus runoff in the watershed. Topology was also a factor in determining the amount of phosphorus concentrations. Regions with steeper inclines and rolling topology had increased levels of particulate phosphorus concentration in the runoff. The type of farming practices also affects the amount of runoff. A study of fields that switched from conventional tillage to conservation tillage found that while the amount of sediment runoff decreased, the phosphorus concentrations increased. This shows that dissolved phosphorus can still enter the watershed and that phosphorus attached to the sediment is not the only source of phosphorus runoff.

The Macatawa watershed area experiences both intense rainfall in the spring and heavy snow in the winter. The goal of this research project is to investigate how snowmelt affect phosphorus levels in the watershed, which will then be compared to rainfall events. The level of phosphorus flux at the beginning of the season will also be compared to the end of the season to determine whether there is a constant release of phosphorus or if the early events have higher level phosphorus flux. The effect of both snowmelt and rainfall have to be fully understood in order to be thoroughly prepared to enact effective remediation techniques.

Methods

Water samples were collected from three locations on the southern branch of the Macatawa River from February 11th to April 22nd. The three sites were just east of I-196/US 31 near Fillmore, Michigan. The area surrounding these sites was dominated by agriculture and most of the land consisted of minimally covered fields, and thus we expected phosphate levels in surface water to respond to snowmelt and rain runoff. The sites were labeled A, B, and C with A being a downstream connection of three tributary branches, Site B corresponding to the western tributary branch, and Site C representing the southern tributary branch as shown in Figure 2. There were two primary objectives for field sampling: to obtain weekly samples to



provide a baseline for phosphate flux during the spring months, and to obtain hourly samples to
Figure 2: Map showing locations of three field sites on the lower branch of the Macatawa River

understand how phosphate concentrations change during snowmelt and rain runoff events. Baseline samples were collected from public access culverts using one liter bottles attached to a pole that could reach the river. To obtain hourly samples, an ISCO automatic sampler was placed at Site A during snowmelt and rain events. The automatic sampler was programmed to collect 24 samples at equal intervals during either 48 or 72 hour periods so samples were taken every 2 or 3 hours. After the samples had been collected they were transferred to 20 mL cuvettes and stored in a refrigerator until they could be analyzed for phosphate concentration.

The samples were then analyzed colorimetrically using methodology derived from Wade and Peaslee (2015). The samples were first spiked with a known concentration of phosphate to ensure they would have a measurable concentration. Next, the samples were mixed with a

solution containing ammonium molybdate and ascorbic acid. Phosphate (VI) ions react with ammonium molybdate to form a purple colored solution that is proportional to the amount of phosphate in the water. Ascorbic acid was added to prevent oxidation during testing. The degree of coloring could then be measured using light spectrophotometry on MicroLab. Each of the samples were tested exactly 20 minutes after they had been combined with the reagent to ensure that they all reacted for an equal amount of time. Three measurements were taken for each sample to ensure accuracy of the MicroLab unit. These samples could then be compared to a standard solution series of known concentration. Absorbance at 620 nm was the primary measurement used to obtain concentrations. The last step to finding concentration was subtracting the phosphate spike to obtain the true concentration of the sample. The concentrations were then combined into baseline samples for Sites A, B and C or into their respective snowmelt or rainfall event and plotted by date in Excel as shown below in the results section. The concentration graphs were compared with stream discharge for the lower Macatawa River from USGS, and temperature and precipitation measurements from Weather Underground. The USGS gauging station was roughly one mile downstream from our field sites, but we expect that our field sites had the same trends as the gauging station.

Results

The compilation of weekly baseline samples taken from February 11, 2016 to April 22, 2016 is shown in Figure 3.

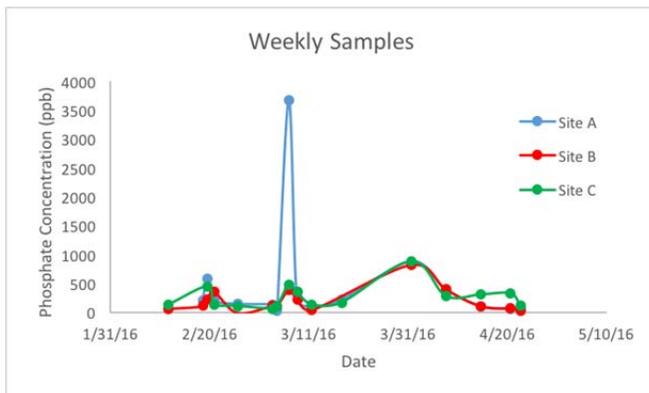


Figure 3. Weekly phosphorus concentrations (ppb) of Site A (blue), Site B (red), and Site C (green) from February 11, 2016 to April 22, 2016.

All three sites followed the same general trend in phosphorus concentration over the sampling period, with one outlier for Site A on March 7, which could have been due to recent activities on that specific surrounding field at that time. The first two peaks were due to snowmelt events and the last two were rainfall events. These events would cause the phosphate levels to peak around 500 - 1000 ppb. Phosphate levels would then return to a baseline level of about 100 ppb, which is still a large concentration for a lake.

The first snowmelt event monitored using the automatic sampler took place on February 21. The sampler was set up to collect every 2 hours for 2 days; however, the hose was displaced due to the rise in water level, so only the first 14 samples (28 hours) were obtained. The change in phosphate concentration during this time is shown in Figure 4.

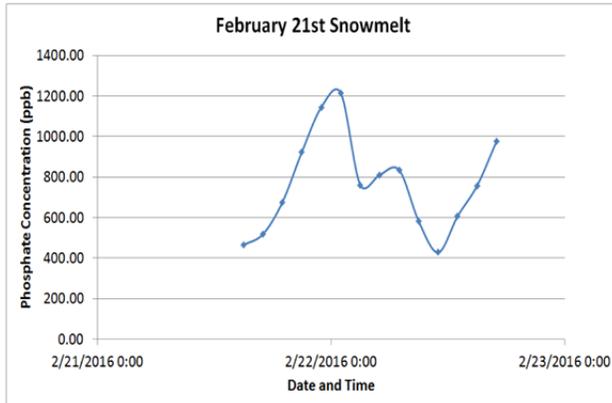


Figure 4. Change in phosphate concentration over 28 hours during the February 21, 2016 snowmelt event.

The phosphate concentration fluctuated between 400-1200 ppb. The highest peak was around midnight on February 22, followed by a secondary peak in the early morning, and a drop again around noon on February 22. Graphs of the discharge rate and temperature during this event are shown in Figures 5 and 6.

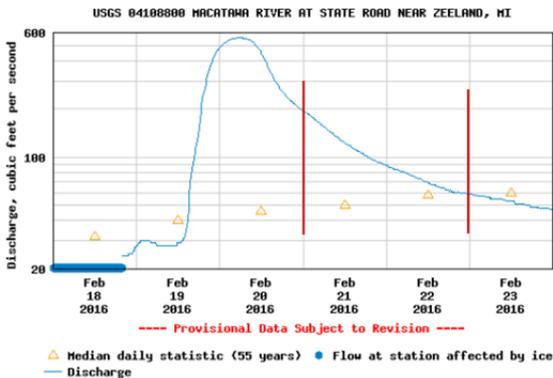


Figure 5. Discharge rate obtained from USGS for the February 21 snowmelt event. The region within the two red lines corresponds to the sampling period.

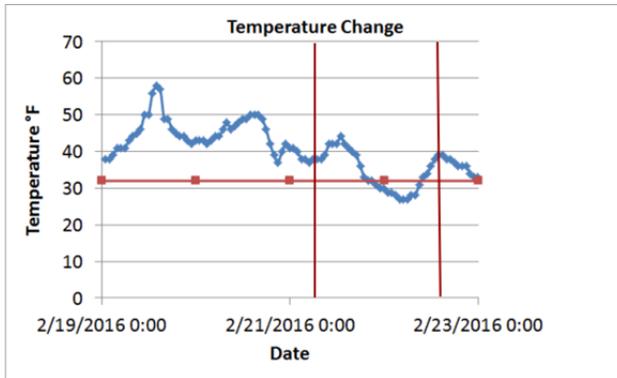


Figure 6. Change in temperature from February 19, 2016 - February 23, 2016. The region within the red lines corresponds to the sampling period.

As seen in Figure 5, only the tail end of the snowmelt event was captured, not the peak. Comparing these figures, there was a delayed response in phosphate concentration to changes in temperature.

The second snowmelt event took place on March 4. The sampler was set up to collect samples every 3 hours over 3 days. The change in phosphate concentration for this event is shown in Figure 7.

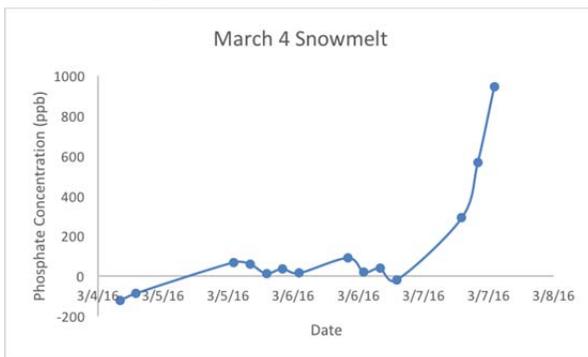


Figure 7. Change in phosphate concentration during a snowmelt event from March 4, 2016 - March 7, 2016.

The phosphate concentration started off around 0 ppb, but then peaked to around 1000 ppb. The discharge rate and temperature over this time period are shown in Figures 8 and 9.

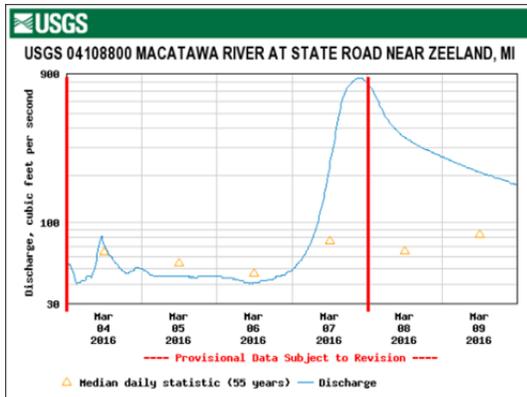


Figure 8. Discharge rate obtained from USGS for the March 4 snowmelt event. The region within the two red lines corresponds to the sampling period.

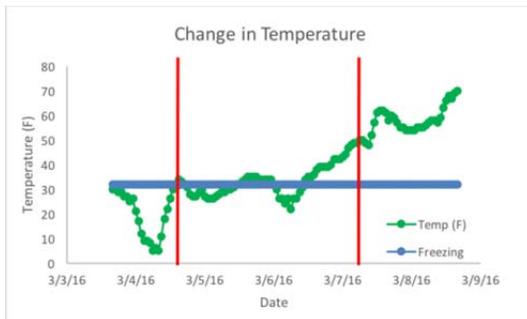


Figure 9. Change in temperature for the March 4 snowmelt event, where actual temperature is shown in green and the freezing point temperature is shown as a blue line. The region within the two red lines correspond to the sampling period.

Phosphate concentration increased with increasing discharge rate and increasing temperature. Similar to the February 21 snowmelt event, there was also a delay in the peak phosphorus concentration. The temperature rose above freezing in the afternoon on March 6, but the peak phosphorus concentration did not occur until the morning of March 7. This delay is due to the time it takes for the snow to melt and for the snowmelt to carry off the sediment and attached phosphorus.

The automatic sampler was set up again on March 8, taking samples every 3 hours. A rainfall event was forecasted during this time period, but not much rain actually occurred. The precipitation during this time totalled 0.04 in. The change in phosphate concentration is shown in Figure 10.

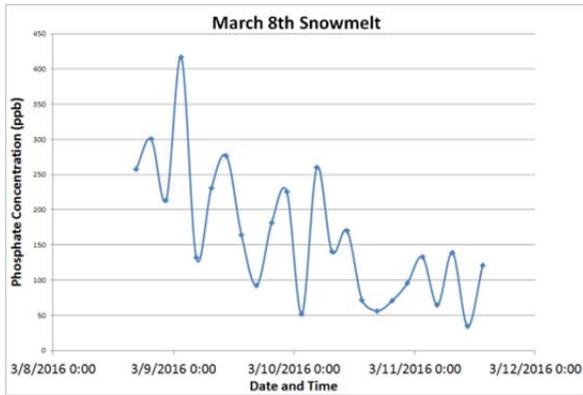


Figure 10. Change in phosphate concentration from March 8, 2016 - March 11, 2016.

The discharge rate and change in temperature are shown in Figures 11 and 12.

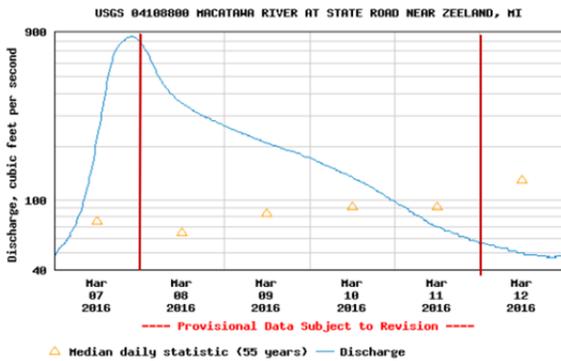


Figure 11. Discharge rate obtained from USGS for the March 8 rain event. The region within the two red lines corresponds to the sampling period.

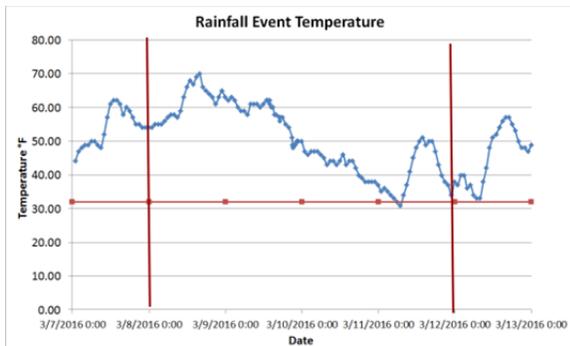


Figure 12. Change in temperature for the March 8 rainfall event, where actual temperature is shown in blue and the freezing point temperature is shown as a red line. The region within the two red lines correspond to the sampling period.

As shown in Figure 11, this sampling period caught the tail end of the March 4 snowmelt event and there was not a significant peak in discharge rate for any precipitation during the March 8 event. Temperatures remained above freezing for the duration of this event. As shown in Figure

10, the phosphate seemed to be released in pulses. There would be a pulse near midnight and another pulse again near mid day.

The final rainfall event captured took place on April 20. The sampler took samples every 3 hours over a period of 2 days. The change in phosphate concentration is shown in Figure 13.

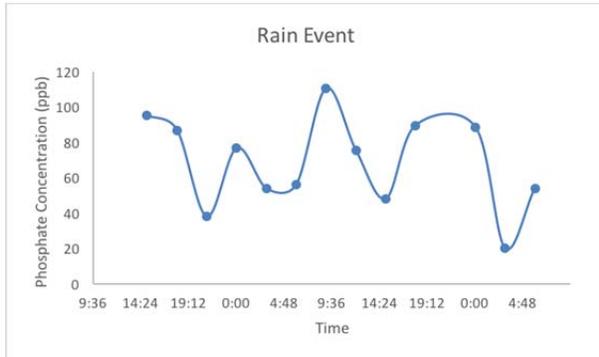


Figure 13. Change in phosphate concentration during a rainfall event from April 20, 2016 - April 22, 2016.

This rainfall event showed a similar pulsing pattern to that shown in Figure 10. This also was not a significant rainfall event. The discharge rate and precipitation are shown in Figures 14 and 15.

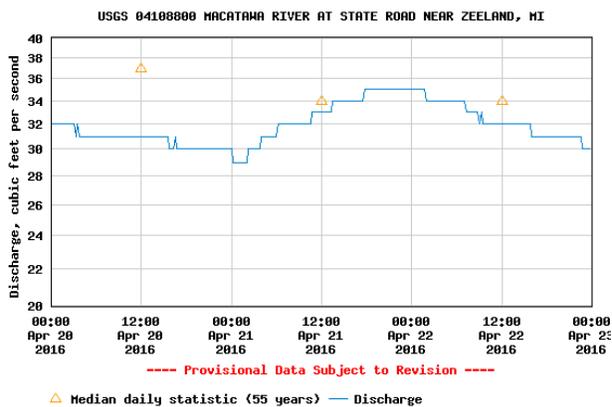


Figure 14. Discharge rate obtained from USGS for the April 20 rain event.

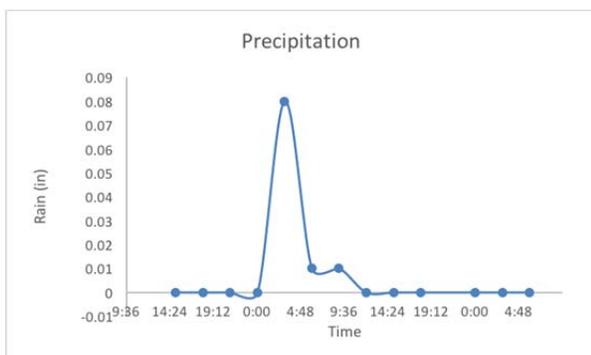


Figure 15. Amount of precipitation (in) during the April 20 rainfall event.

Temperature during this time remained above freezing, so change in temperature was not significant during this sampling event. As shown in Figure 13, the phosphate level would fluctuate between 20-120ppb, which is much lower than the snowmelt events. This could be due to the size of this rainfall event. There was about a tenth of an inch of rain and the discharge rate only increased by about 10ft^3 . The small rainfall events compared to the snowmelt events demonstrate that the amount of water influences the phosphate flux.

Discussion

Our results show that baseline concentrations of phosphate in the lower Macatawa River were around 100 ppb at our three field sites. These values are significantly above the healthy range of 25-50 ppb indicating that these sites likely contribute to eutrophication of Lake Macatawa. During the snowmelt events we observed, discharge drastically increased by over an order of magnitude and phosphate concentration raised to over 1000 ppb. Previous studies have found that the phosphate concentration released through runoff is related to the amount of water released during snowmelt or rainfall events. Our measurements supported this theory because the highest phosphate concentrations corresponded with the earliest snowmelt event we measured where over a foot of snow had accumulated in the previous weeks. Snowmelt runoff generally had higher concentrations than rain runoff, as our rain events had concentrations of 100-400 ppb. However, one baseline sample was taken on March 31st one day after a major rain event and had a concentration of 1000 ppb which is comparable to snowmelt runoff.

Further study is needed to determine how phosphate concentration changes throughout the entire year. The scope of our study was fairly limited, so expanding samples to upstream and downstream locations would be useful to assess how concentration changes throughout the Macatawa Watershed. Farmers in the area should consider adding cover crops or buffer strips to maintain nutrient levels in their fields, and mitigate eutrophication within the watershed. Overall our study supported the idea that phosphate concentration is related to the amount of water released during runoff events. Our findings show that even baseline phosphate concentrations between runoff events are still high enough to contribute to eutrophication, and runoff causes drastic increases in phosphate concentration which needs to be addressed to improve water quality within the Macatawa Watershed.

References

1. Macatawa Watershed Project. The-macc.org.
2. Jensen, T.; Tiessen, K.; Ester, S.; Kalischuk, A.; Flaten, D.N. 2011. Spring Snowmelt Impact on Phosphorous Addition to Surface Runoff in the Northern Great Plains. *Better Crops*, 95, 28-31.
3. Su, J.J.; van Bochove, E.; Theriault, G.; Novotna, B.; Khaldoune, J.; Denault, J.T.; Zhou, J.; Nolin, M.C.; Hu, C.X.; Bernier, M.; Benoy, G.; Xing, Z.S.; Chow, L. 2011. Effects of snowmelt on phosphorus and sediment losses from agricultural watersheds in Eastern Canada. *Agricultural Water Management*, 98, 867-876.
4. Tiessen, K.H.D.; Elliott, J.A.; Yarotski, J.; Lobb, D.A.; Flaten, D.N.; Glozier, E. Conventional and Conservation Tillage: Influence on Seasonal Runoff, Sediment, and Nutrient Losses in the Canadian Prairies. 2010. *Journal of Environmental Quality*, 39, 964-980.
5. Peaslee, G. Spring Precipitation vs. Ave. Phosphate from 1997-2005
6. Peaslee, G.; Wade, R. Phosphate Lab, Biology & Chemistry 195.
7. http://waterdata.usgs.gov/nwis/uv?site_no=04108800
8. <https://www.wunderground.com>