Internal Loading, Big Lake, Polk County, WI, WBIC: 2615900 2018

J. Williamson, Polk County Land and Water Resources Department

In shallow lakes there is intense interaction at the water sediment interface. Therefore, understanding sediment water interactions is crucial to understanding the nutrient dynamics of shallow lakes such as Big Lake (Scheffer, 1998). The sediments demand for oxygen is high as it is broken down by microbial communities. At the sediment surface, a difference of a few millimeters in oxygen penetration is the critical factor regulating exchange of nutrients and inorganic elements such as iron between the sediment and water. Under aerobic conditions, the exchange is largely from the water to the sediment. Under anaerobic conditions, however, phosphorus can move from depths up to 10 cm deep and be released into the water column (Wetzel, 2001). An analysis of the hypolimnetic nutrients of Big Lake has implications for best management actions in 2016 to 2018.

The most significant form of inorganic phosphorus is orthophosphate. Much emphasis has been placed on the evaluation of the nutrient phosphorus because of its fundamental importance in lakes systems. The types of phosphorus commonly evaluated are soluble reactive phosphorus, soluble unreactive phosphorus, particulate reactive phosphorus, and particulate unreactive phosphorus (Wetzel, 2001). Often analysis is done for total phosphorus.

A substantial source of available phosphorus in shallow lakes, such as Big Lake, is the sediment. Release of phosphorus from the sediment into the water column depends on the composition of the sediment and the concentration of the phosphorus in the water column. Phosphorus release can vary strongly depending on the conditions at the sediment water interface (Scheffer, 1998) (Kaiserli, A., Voutsa, D., and Samara, C., 2002) (Gonsiorczyk, T., Casper, P., and Koschel, R., 1998).

Phosphorus found in the sediments of lakes is often precipitated with clays, aluminum, and iron compounds. Work on Wisconsin lake sediments and the Great Lakes indicate that phosphorus in the sediments is predominately apatites (phosphate minerals), organic phosphorus, and orthophosphate bonded to iron compounds. However, as the oxygen content near the sediment declines, there is a release of phosphorus, iron, and manganese to the water column (Wetzel, 2001).

The concentration of phosphorus in the water column tends to correlate well with the ratio between phosphorus and iron concentrations (P:Fe) in the sediment. It has been found where the P:Fe ratio is lower than 1: 10, the correlation with lake water becomes weak (Scheffer 1998). The ratio of P to Fe in the hypolimnetic water of Big Lake ranges from 3:1- 1:32 indicating a strong correlation between the sediment P pool and the water column phosphorus concentration during certain times. The mobilization of recently deposited P seems to be the driving force of P-release in eutrophic lakes such as Big Lake (Gonsiorczyk et.al. 1998). However, there is a limited amount of knowledge of the mechanisms behind internal loading in shallow lakes (Søndergaard et.al., 2001). Water



Figure 1. Hypolimnetic total phosphorus in Big Lake, 2016



Figure 2. Hypolimnetic total phosphorus in Big Lake, 2017

samples analyzed from near the water-sediment interface do indeed show an increase in phosphorus during the open water season, indicating an internal release of P.



Figure 3. Hypolimnetic total phosphorus in Big Lake 2018

Internal P-loading may delay the recovery of a lake once the external P-loading sources are reduced; therefore it is important that the fraction of available phosphorus (iron and manganese bound) is evaluated for predicting internal P-loading. The major factors controlling P release are dissolved oxygen, nitrates, sulfates, and pH (Kaiserli et.al., 2002).





Figure 5. Hypolimnetic soluble reactive phosphorus in Big Lake 2017





Concentrations of nutrient binding elements, such as iron, depend greatly on the redox potential of the sediment. A redox reaction is the flow of electrons between an oxidized and reduced state (for example iron moving from Fe^{3+} to Fe^{2+} and vice versa). The state of these elements is very important for the ability to bind to nutrients, particularly phosphorus (P). Iron is a very important micronutrient in aquatic systems. It is essential for aquatic organisms in many ways including: electron transport in oxidation-reduction systems of photosynthesis and respiration, it can be responsible for enzyme activation, and an oxygen carrier in nitrogen fixation in cyanobacteria (blue-green algae).

Iron exists in solution in two different forms; either ferrous (Fe^{2+}) or ferric (Fe^{3+}). The amounts of iron in solution in lakes and the rate of oxidation of Fe²⁺ to Fe³⁺ that is oxygenated water are dependent on pH, reduction potential, and temperature. Ferrous iron tends to be more soluble than ferric. Under anaerobic conditions with low redox potential, in productive lakes (such as Big Lake) bacteria often reduce sulfate to sulfide which decreases the concentration of Fe^{2+} through the formation of insoluble FeS. This, iron sulfide formation can reduce the abundance of Fe compounds that can complex to phosphorus and promote release of phosphorus from the sediment (Wetzel, 2001). If enough FeS precipitates enough Fe can be removed which results in iron poor water making phosphorus more available for algae uptake. This is sometimes called the Sulfur Trap.

Sulfur Trap for Iron

anoxic sediments

HS- diffuses upward when reaches Fe2⁺:

Depth in sediment

 $Fe^{3+} \rightarrow Fe^{2+} \text{ iron reduction}$ $SO_4^{2-} \rightarrow S^{2-} \text{ sulfate reduction}$ $Fe^{2+} + S^{2-} \leftrightarrow FeS$

FeS is insoluble and precipitates out of solution

Figure 7. The sulfur-iron trap

Iron bonds (complexes) with many organic compounds (e.g. detritus), which greatly alters the solubility and availability to organisms. Under anoxic conditions in the surface sediment and overlying water these complexes are reduced and phosphorus is released. The release rate from sediments doubles if the sediments are disturbed (though activities such as power boating for example) (Wetzel, 2001). However, the oxygen concentration and temperature of the water column of Big Lake seem to remain



Figure 8. Dissolved oxygen profiles Big Lake 2016, deep hole

Temperature profiles, however remain consistently mixed.



Figure 9. Dissolved oxygen profiles Big Lake 2017, deep hole



Figure 10. Dissolved oxygen profiles Big Lake 2018, deep hole



Figure 11. Dissolved oxygen profiles Big Lake 2017, near the landing



Figure 12. Dissolved oxygen profiles Big Lake 2017, near the North Creek Inlet





Temerature 2017 Deep Hole —6/7/2017 **Depth (m)** 2 2 2 **—**7/19/2017 **—** 8/28/2017 **9/12/2017 —9**/24/2017 **—**10/12/2017 °C









Figure 16. Temperature profiles Big Lake 2016, near the landing



Figure 17. Temperature profiles Big Lake 2016, near North Creek

Figure 18.

Hypolimnetic iron

concentrations in

Big Lake, 2016

Constant mixing could significantly add to the internal load even during sort periods of anoxia. For instance, there appears to be a significant release event around mid-July in 2016 and 2017, and a study increase throughout the growing season in 2018.





Figure 19. Hypolimnetic iron concentrations in Big Lake, 2017





Sulfur is utilized by all living organisms in both inorganic and organic forms. Sources of sulfur compounds to natural waters include solubilization from rock, fertilizers, precipitation and dry deposition. Most (about 90%) of the total sulfur content in lake basins is found in the organic matter of mineral soil. Therefore much of the loading of sulfur compounds to lakes is in the form of sulfate and soluble organic sulfur compounds (Wetzel, 2001).

The cycling of sulfur entails the different sulfur chemical species under various conditions, the biotic influences, and sulfur transport within the lake. The predominant form of sulfur in water is sulfate; nearly all assimilation of sulfur is as sulfate.

Sulfur that reacts with metals to form metal sulfides are extremely insoluble, so when Fe^{+2} is released from the sediment, it reacts vigorously with S to form FeS. Because the FeS is so insoluble iron is not available to bind with phosphorus (Wetzel, 2001). This appears to be occurring in Big Lake in 2016, sulfate concentrations go down significantly after what appears to be a release of iron from the sediment on July 5th. However, the hypolimnetic sulfate concentrations appear to be trending upward in the 2017 data set, and downward again in the 2018 dataset.



Figure 21. Hypolimnetic sulfate concentrations in Big Lake, 2016



Figure 22. Hypolimnetic sulfate concentrations in Big Lake, 2017



Figure 23. Hypolimnetic sulfate concentrations in Big Lake, 2018

The data collected over the last three open water seasons gives the appearance that there is likely internal loading events occurring in Big Lake during periods of the summer particularly in mid-July. There was very little evidence on anoxia during the 2016 sampling events, while there was approximately 120 days of anoxia during the 2017 sampling season. Yet, the phosphorus dynamics of 2017 do not show the study upward trend of the 2016 samples and instead show a spike in mid-July that correlates with a spike in iron and a slight decrease in sulfate. In 2018 there appears to be a slight decrease in total phosphorus, but a steady increase in dissolved reactive phosphorus. Because the sampling data between all years were very different the data points were combined and analyzed using the statistical program R to explore relationships between the various parameters. The different sampling parameters were bootstrapped and resampled and then compared to each other in linear models and generalized linear models. The R squared value of the models ranged from 0.20 to 0.08 with the relationship of iron to the combined dataset of phosphorus and sulfate being the strongest.



Figure 24. Example of generalized linear model of Fe to TP + SO₄

Because the linear models showed such poor correlation an analysis of variance (ANOVA) was performed on the models and Welch Two Sample t-tests were performed on the data as well comparing the different variables. The ANOVA tests did not show significance in the models (which is to be expected based on the R² values. The t-tests were used similarly to the models. The p-value of the t-test were all significantly below 0.01, meaning there is very little correlation to the different variables to each other.

In a final effort to find relationships of the different variable to each other a principal component analysis was performed. A principal component analysis is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components.



Figure 25. Principal component analysis ordination plot of variables sampled in Big Lake hypolimnion.

The first two principal components of the analysis explain 67.4% of the variation in the samples when compared to each other. The ordination also shows that Fe is orthogonal to SO₄, meaning they are not related. Meanwhile, TP and SRP is not close to the other variables. This indicates that when all there datasets are combined that internal loading may not be a factor.

When the data is used to model internal loading from the sediment it suggests a significant net internal load as part of the nutrient budget. Net internal load (L_{int-1}) consists of sediment released P that is diminished by subsequent settling. Gross internal load (L_{int}) is the total quantity of sediment released P using the equation:

$$L_{int-1} = (P_{t_2} \times V_{t_2} - P_{t_1} \times V_{t_1}) / (A_o),$$

Where t_1 is the initial date and t_2 is the date at the end period (Julian day), P_t is the correspondent P concentration, and V_t is the correspondent lake volume, and A₀ is the lake surface area. The internal load was predicted to be 202 kg (445 lbs.) or 55.3 percent of the load in 2016. When the model is applied to the 2017 data the internal load is predicted to be 80kg (176 lbs.) or 21.8 % of the phosphorus load in the lakes nutrient budget. When the model is applied to the 2018 data the internal load is predicted to be 13.6kg (80 lbs.) or 6 % of the phosphorus load. This model uses *in situ* increases of P concentration throughout the summer period. Because lake levels were not monitored in 2016, 2017, or 2018 they were not considered (Nürnberg et al 2012).

The epilimnetic response to the release of sediment phosphorus appears to be negligible. The pool of phosphorus released from the sediment does not seem to be making an impact on the epilimnetic phosphorus concentrations. In 2016 the Totoal phosphorus (TP) ranged from $17\mu g/l$ to $39.6\mu g/l$. The lowest reading was on July 21^{st} , meaning that particulate phosphorus may have been lost from the epilimnion due to sedimentation. In 2017 the TP reading ranged from $23 \mu g/l$ to $34.3 \mu g/l$, again with the lowest result occurring in July (July 24^{th}). In 2018 the lowest reading was also in July (July 23^{rd} , $15.1 \mu g/L$).



Figure 26. Bubble graph of epilimnetic phosphorus in Big Lake 2016 - 2017

The chlorophyll *a* data is also quite variable between years (although sampling was minimal). In 2016 there was a steady increase in chlorophyll *a* from 8.72 μ g/l on June 17th to 24.1 μ g/l on September 5th. In 2017 there was a decrease in chlorophyll *a* from 4.08 μ g/l on June 21st to 1.92 μ g/l on August 28th. Chlorophyll a dynamics could be largely influenced by cyanobacteria nitrogen fixation and also the spring and fall diatom maximums. 2017 Has a very long winter and a very late ice out compared to 2016. Long term data analysis is invaluable to tease out anomalies like this. 2018 had a very steady, almost analogous, chlorophyll readings.



Figure 27. Bubble graph of chlorophyll *a* in Big Lake 2016 - 2018

Additionally the relationship between phosphorus and chlorophyll *a* appears to be quite anemic in the data that was collected through the Citizen Lake Monitoring Network (CLMN). When chlorophyll *a* is plotted against phosphorus there is a very weak relationship. This could be due to nitrogen fixation or a number of other factors that were not monitored in this study.





When the internal load estimates are used in a nutrient budget for the lake calculate the lakes phosphorus budget there is also considerable variability. In 2016 the estimated contribution to the phosphorus budget was 445 pounds of 46% of the nutrient budget.

In 2017 the internal load was 176 pounds or 25% of the phosphorus budget and in 2018 it was only estimated to be only 30 pounds or 6% of the phosphorus budget. This annual and seasonal variability could be overcome by doing incubation experiments in a lab setting.



Figure 29. 2016 Big Lake nutrient budget



Figure 30. 2017 Big Lake nutrient budget



Figure 31. 2018 Big Lake nutrient budget

The data collected, the statistical models, the empirical models, epilimnetic response, and calculated nutrient budgets all indicate that the internal loading component of the nutrient budget **could** very significant at times but is likely both seasonally and annually variable. The senescence (dying back) of *Potamogeton crispus* (CLP) may contribute slightly, but likely the main release mechanisms is the release of phosphorus bound to iron because of changes in redox potential at the sediment water interface and sediment resuspension and changes in the water budget due to the drying up of the outlet of the lake. Groundwater could be a source of phosphorus mid to late summer as the lake's residence time changes.

Because of the potential importance of the sediment phosphorus pool in Big Lake the author still believes further study of sediment release is warranted. In situ sediment release rates should be measured with incubation chambers and data should be continued to be collected over a series of years in several locations to accurately calculate actual P release from the sediment. In addition, sediment cores should be collected and species of phosphorus should be fractioned using sequential extractions (Engstrom and Wright, 1984). Water column phosphorus can be reconstructed using diatoms, hypolimnetic oxygen concentrations can be reconstructed using chironomid head capsules, and cyanobacteria (blue-green algae) communities can be reconstructed with the use of fossilized pigments (Williamson et al, 2016) (Juckem and Robertson 2013). The timing and magnitude of change is unknown and should be under study before consideration of sediment amendments such as alum or other drastic management techniques are used. In addition, an analysis of stable isotopes deuterium (D or ²H) and oxygen 18 (¹⁸O) would greatly increase our understanding of how the landscape and ground water influence the nutrient budget of Big Lake and possibly influence management decisions.

References

- Engstrom, D. R. & Wright, H. E. (1984): Chemical stratigraphy of lake sediments as a record of environmental change. In: Haworth, E. Y. & Lund J. W. G. (eds): Lake Sediments and Environmental History. Leicester University Press, Leicester, pp. 11–68
- Gonsiorczyk, T., Casper, P., and Koschel, R. (1998). Phosphorus-Binding Forms in the Sediment of an Oligotrophic and an Eutrophic Hardwater Lake of the Baltic Lake District (Germany). *Wat. Sci. Tech., 37*(3), 51-58.
- Juckem, P. J., and Robertson, D.M. 2013 Hydrology and water quality of Shell Lake, Washburn County, Wisconsin, with special emphasis on the effects of diversion and changes in water level on the water quality of a shallow terminal lake: U. S. Geological Survey Scientific Investigation Report 2013-5181, 77 p., 2 app., <u>http://dx.doi.org/10.3133/sir20135181</u>.
- Kaiserli, A., Voutsa, D., and Samara, C. (2002). Phosphorus Fractionation in Lake Sediments--Lakes Vovi and Koronia, N. Greece. *Chemosphere, 46*, 1147-1155.
- Nürnberg, G. K., Tarvainen, M., Ventela, A., and Sarvala, J. (2012). Internal phosphorus load estimation during biomanipulation in a large polymictic and mesotrophic lake. Inland Waters, 2, 147-162
- Søndergaard, M., Jensen, J.P., Jeppesen, E. (2001). Retention and internal loading of phosphorus in Shallow, Eutrophic Lakes. *The Scientific World, 1*, 427-442.
- Scheffer, M. (1998). Ecology of Shallow Lakes. London: Chapman & Hall.
- Wetzel, R. G. (2001). *Limnology Lake and River Ecosystems Third Edition.* San Diego, California: Academic Press.
- Williamson, J., Edlund, M. B., and Ramstack Hobbs, J., and Burge, D. R. L. 2016. A Paleolimnological Study of Big Blake Lake, Polk County, Wisconsin. Final Report to Big Blake Lake Protection and Rehabilitation District. Polk County Land and Water Resources Department, Balsam Lake, WI.