

Pre and Post Settlement Nutrient and Heavy Metal Levels in Lake Sediments, Spring Lake, MN

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Abstract

Humans have a large impact on the environment that surrounds them, including our lakes and waterways. I set out to find how people were affecting the nutrient and heavy metal levels that were being introduced into Spring Lake, a hyper-eutrophic lake and part of a large watershed in Prior Lake, MN where water quality is a big concern. To measure the amount of environmentally available phosphorus that was locked in the sediments I used a multi-step acid digestion method and then used ICP-AES to determine P, Pb and As concentrations. Total organic carbon and nitrogen concentrations were measured as well throughout the core and smear slide analysis was done to figure out what type of environment and water conditions were present during the deposition of the sediments. Pb-210 dating allowed us to make age profiles for our record and we discovered that in the 1920's there began to be an increase in the accumulation rates of our elements of interest. The depositional rates of all of our elements of interest increased two to seven times after the 1920's. Phosphorus, the main element of focus, had an accumulation rate of .28 $\mu\text{g}/\text{cm}^2\text{yr}$ in 1885 and increased to 1.45 $\mu\text{g}/\text{cm}^2\text{yr}$ by 1982. This correlates to when settlement in the area began and gives us a better understanding of how the development and growth of the urban area has affected the state of Spring Lake. With all this new information we can now understand how the nutrient and contaminant inputs have been affected in the past, which will help the Prior Lake/Spring Lake watershed be able to manage it better in the future.

Introduction

Spring Lake is a dimictic, 580-acre Lake with a maximum water depth of 37 feet and has average water clarity of 1.9 feet. It has a 13,500 acre watershed and currently feeds water into Upper and Lower Prior Lake. Spring Lake is a highly used recreational lake and has had problems with its aesthetic quality because of eutrophication.

Eutrophication occurs when there is an increased amount of nutrients and primary productivity, commonly due to anthropogenic pollution that creates nutrient inputs from sewage draining and agricultural runoff. Eutrophication can lead to dangerous algal blooms and when they start to decay they begin using up the dissolved oxygen in the water, creating hypoxic conditions. Without sufficient dissolved oxygen in the waters, plants and animals may begin to die off in large numbers. In the last two years Spring Lake has witnessed two seasonal fish deaths that occurred in June of

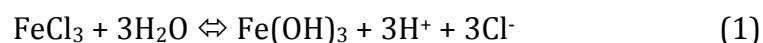
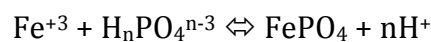
2008 and June of 2009 and were species-specific to black crappies. These events are most likely due to a bacterial disease called *columnaris*, which is prevalent where high bio-loads exist or when there is low dissolved oxygen in the waters. This would be an expected result of eutrophication, which is presently occurring in Spring Lake. [1]

Many studies have been done in the past to understand how eutrophication occurs and what the best ways to prevent it are. Early laboratory results suggested that eutrophication was caused by several nutrients, mainly phosphorus, nitrogen and carbon. In the early 1970's Canada's ELA (Experimental Lakes Area) research group was studying the effects of these three nutrients and found that eutrophication could successfully be controlled by just one of these nutrients, phosphorus. [2]



Figure 1: A plastic curtain divider separated this lake. The upper clear area of the lake with no visible algal blooms had only Carbon and Nitrogen added to the lake. The lower green/scummy area had the additions of Carbon, Nitrogen and Phosphorus added to the lake showing the effects of Phosphorus on the system.

The Prior Lake/Spring Lake watershed has been attempting to reduce phosphorus levels in Spring Lake for over a decade. Multiple remediation techniques have been done but few have shown a large-scale change in phosphorus levels in the waters or sediments. They currently are managing the curlyleaf pondweed and benthivorous fish populations because of the excessive amounts of phosphorus they re-introduce into the lake waters annually. From 1999-2002 Ferric Chloride was added into County Ditch 13, a major tributary to Spring Lake. FeCl works as a coagulant that binds with the phosphorus and precipitates it out of solution taking it out of the water column and allowing it to settle in the sediments.

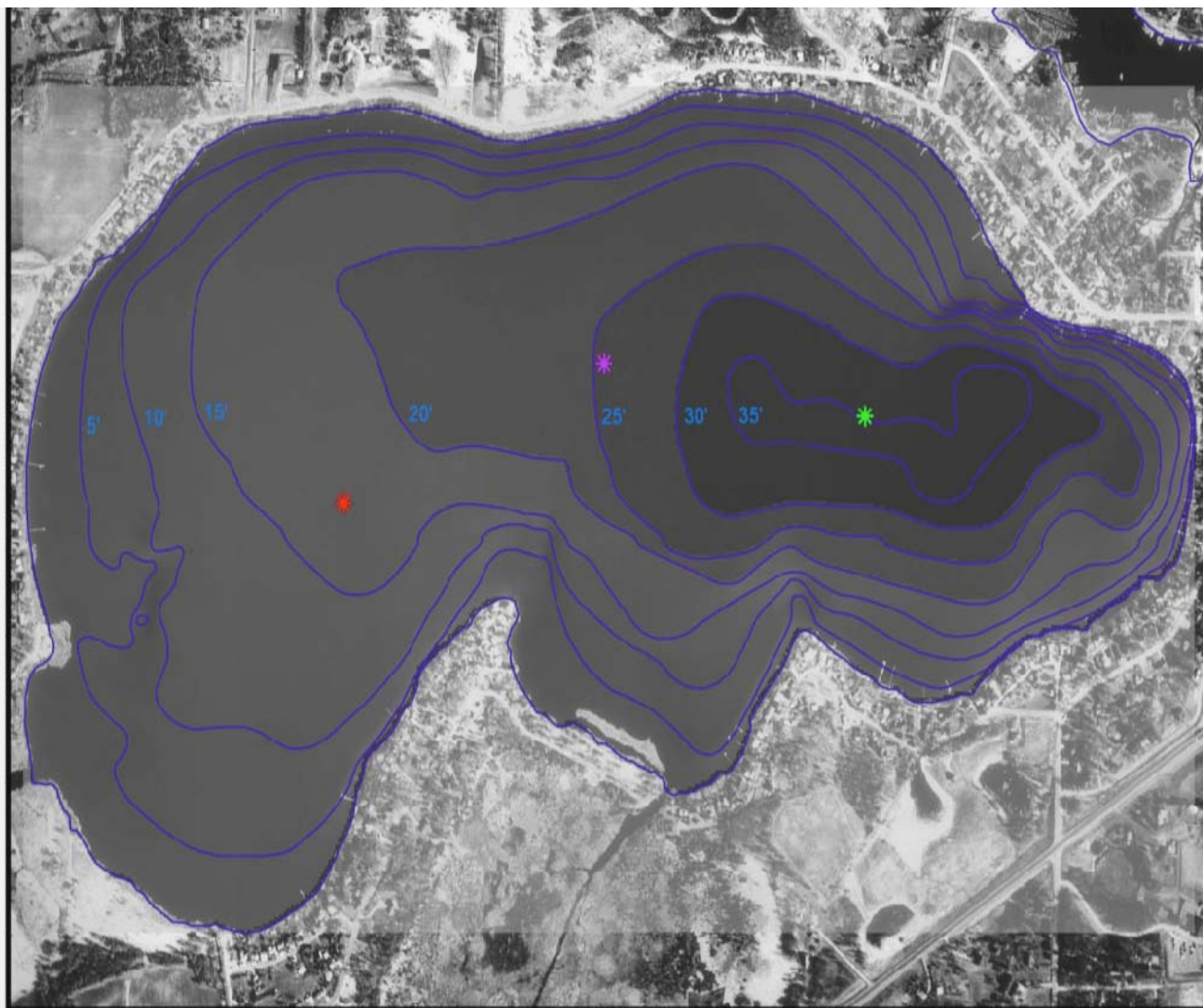


The treatment system reduced the total phosphorus by 30% and the dissolved phosphorus by 45% but initial goals set out for the treatment system were not reached so the treatment did not continue after 2002. During the study they also found that more suspended solids were put back into the water column and internal loading contributes to 43%-78% of the total phosphorus load in Spring Lake. [3],[4], [5]

Spring Lake is in jeopardy and is on track to become a public nuisance because if the phosphorus levels are not controlled there will be a good chance that excessive nutrients will spread to the Upper and Lower Prior lakes. This could reduce the real estate, recreational and aesthetic value of the lakes, which could create a problem with the regional economy. I set out to find how the phosphorus levels have changed historically and to understand how big of an impact human settlement has had on these levels. I also wanted to see if the remediation efforts made by the PLSL watershed have had any direct impact on the phosphorus levels deposited in the sediments.

Methods

Collecting sediment cores. To collect the cores to use for analysis I went out with my advisor Dr. Kevin Theissen and Dr. Amy Myrbo from the University of Minnesota's Limnological Research Center (LRC) in June of 2009. We took out their 20-foot pontoon boat with a moonpool cut in the floor and used a Bolivia coring system to collect the core. The Bolivia coring system is a modified Livingston corer, which is a drive rod piston corer that can core in lakes up to 30 meters deep. Four cores were taken that day at three different sites. Three were taken back to the LRC laboratory and split into halves and then imaged at high resolution. Magnetic susceptibility data was recorded so that future work and correlations between the cores could be done. The fourth core was extruded on site at 1cm resolution and this was the core that was used for my analysis. I created a bathymetric map using ArcGIS and input the GPS coordinates to indicate where each core was taken from Spring Lake. The purple star on the map represents the core that was used for analysis. The reason this coring location was chosen for analysis is because it would be least affected by large storm events or slump features which could be present in the shallow (red) and deep (green) cores. **(Figure 2)**



Legend

- * PLSL-STP09-3A
- * PLSL-STP09-2A:210Pb Dating Core
- * PLSL-STP09-1A
- 5 Foot Intervals



Figure 2: Spring Lake bathymetric map with site locations of core samples collected.

Pb-210 Dating. To prepare the sediment for Lead-210 dating I first needed to measure the L.O.I (Loss on Ignition). The samples were homogenized and 2 cc aliquots were weighed and labeled and then placed in aluminum tins. The samples were heated to 100 degrees Celsius for 24 hrs and weights were recorded to get the amount of water in the samples. The samples were then heated to 550 degrees Celsius in a muffle furnace for 4 hrs and weights were recorded to get the amount of organic material that was present in the sediments. After this data was collected I

was able to run it through a macro in Excel that was created by Dr. Daniel Engstrom of the St. Croix Watershed Research Station (SCWRS). This macro gave us the dry and wet densities, dry to wet ratios and organic to inorganic percentages. Pb-210 age dating is very useful in getting an age date for the last 100-200 years. Pb-210 is a naturally occurring radioisotope that is created from the ^{238}U -decay series and has a 22-year half-life. Samples are measured stratigraphically throughout the core and continue until the Pb-210 isotope is no longer measurable in the sample (approx. 5-8 half lives). After you have comprised a Pb-210 profile a mathematical model is applied that creates a linear Pb-210 accumulation profile and the results give you actual age dates for your samples. All of the Pb-210 age dating samples were sent off to SCWRS where they were able to get age dates for the core.

Smear Slide Analysis. To analyze the compositions of the sediments smear slide analysis was done at each horizon within the core. Looking at the slide under a microscope and analyzing the coverage on the slide I was able to determine biogenic, clastic and chemical percentages. To make a smear slide a small aliquot was spread evenly across a glass slide and then placing the slide on a hot plate evaporated the water and you were left with a glimpse of the composition at that horizon. Environmental conditions can be determined by the absence or presence of different proxies like diatoms or ostracods.

Flash EA analysis of TOC and Nitrogen. For C/N analysis sediments were dried in an oven at 60 degrees Celsius and then ground to powder and homogenized with a mortar and pestle. Once samples are homogenized we can begin to prepare them for the FlashEA 1112 Organic Elemental Analyzer, which combusts the sediments at high temperatures and measures the amount of CO_2 and Nitrogen gas that is produced giving us % analysis of the TOC and N in a sample. Nitrogen analysis was done using 10x12mm tin capsules and a Mettler Toledo UMX2 microbalance to measure approx 4 mg of sediment. These samples were then pressed and folded and made ready for analysis in the FlashEA 1112. Sulfurous acid was added to the samples that were being measured for total organic carbon to get rid of any inorganic carbon in the samples. Aspartic acid was used as a laboratory standard and blanks were also included to increase the precision and accuracy of analysis.

Multi-Step Acid Digestion. To get the elements of interest out of the sediments I used a modified EPA Method 3050B. This was a partial digestion and I used a hot bath instead of a hot block digester. This method targeted the environmentally available phosphorus but fails to digest the silicate bound phosphorus. Multiple additions of acid and peroxide were added to the sediments and after each addition the sample was heated, refluxed and cooled. After multiple steps the sample was filtered and a solution with our elements of interest was obtained. [6]

Inductively Coupled Plasma–Atomic Emission Spectroscopy Elemental Analysis. To measure the total elemental concentrations of P, Pb and As I used the ICP-AES in the UST Geology Laboratory. This machine excites electrons and

measures the intensity of electromagnetic radiation emitted which correlates to different elements. The intensities will map against an intensity curve and give concentrations back.

Results and Interpretation

By looking at the smear slide analysis we are able to see a few key changes in the lake. Around 1925 there was a switch from the deposition of organic rich sediments to a more diatom- dominated sediment. Diatoms are more abundant when there is an increased input of nutrients and at this horizon there was an increased abundance by 7 times. We can also see that from 2002 to 2007 laminations began to form; laminations indicate periodic shifts and show a time of anoxia. The figure below shows the different sediment horizons and their diatom percentages.

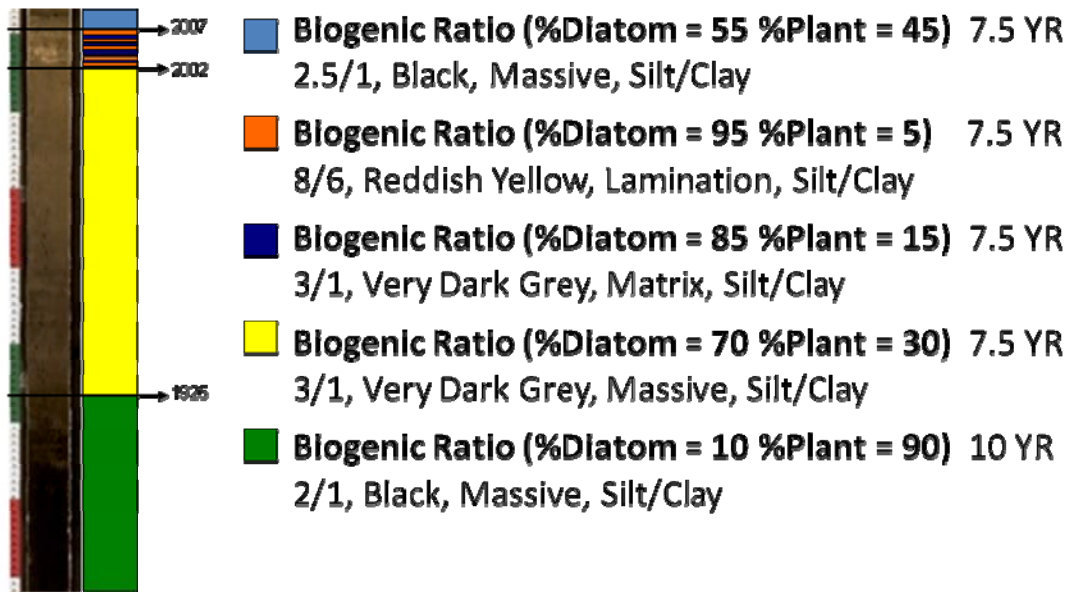


Figure 4: Smear Slide Analysis

Below are results for the total organic carbon and nitrogen results. As you can see from the graphs there are four main shifts in the lake sediment accumulation rates. From the early 1800's to 1920 there is a stable accumulation rate and then after the 1920's to 1980 we see a gradual increase to approximately three times the original values. There is a steep decrease for approximately the next ten years and then another rise that brings accumulation rates back up to their original maximum values. All of these events seem to have some historical event related to them. The blue represents the early 1800's to 1920 when there was very little growth around the spring lake area and there wasn't a large amount of anthropogenic pollution running off into the lake. The area started to grow after the 1920's and population went from a few hundred to over seven thousand in 1980 creating more runoff and pollution into the lakes this era is represented by red on the graph. Green

represents the 1980's when America went through an event called the Farm Crisis. During the late 1970's and early 1980's many farmers lost their farms or were influenced by a bad economy and many other factors. This crisis could be one explanation for the decreased amount of carbon and nitrogen runoff because of a decrease in regional agricultural practices. Around 1990 the economy cycled back and there was a large-scale development boost in the area of Spring Lake with little regulations of soil erosion, which would explain the increased rates of carbon and nitrogen and is represented by yellow on the graph.

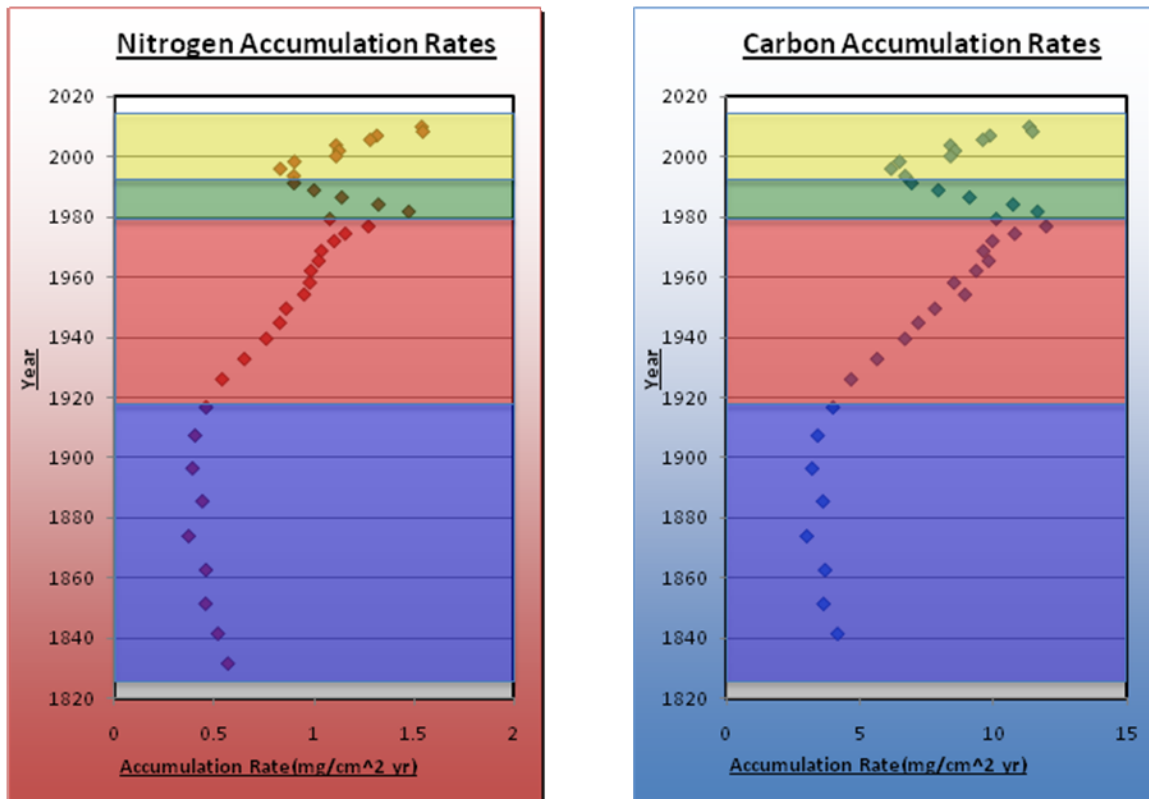


Figure 5: Nitrogen and Carbon Accumulation Rates

With the nitrogen and carbon percentages I was also able to find the C/N ratio, which works as a proxy relating to the type of plants being deposited. The graph below shows the C/N ratio through time. Higher C/N values relate to a more terrestrial plant input and lower C/N values relate to a more algal dominated lake. By observing the blue section of the graph we see that Spring Lake historically has always been an algal dominated lake but around 1920 we see a small shift in terrestrial input which is represented by the red highlighted area. This section is representative of when development of the area began where there was likely an increase in terrestrial runoff from the development in the area. Then after the 1950's we see another shift into a more terrestrial dominated input into the lake, which is represented by the green section on the graph. This section is most likely due to the implementation of moldboard tilling in the area, an agricultural practice

that essentially flips the crops over exposing soil that is easily erodible which would create a greater amount of runoff in the area into local streams and tributaries. After the 1980's we see a sharp decrease in C/N ratios into a much more algal dominated community, which is represented by the yellow section. I believe that this is due to the farm crisis, which would create less agricultural runoff into the lake. Around 1990 we see an attempt to rise back to previous high values but it fails to do so; I hypothesize that after the farm crises Spring Lake went through a shift where it became extremely algal dominated and any increase in terrestrial input that occurred after 1990 was muted by the excessive amount of algae being deposited.

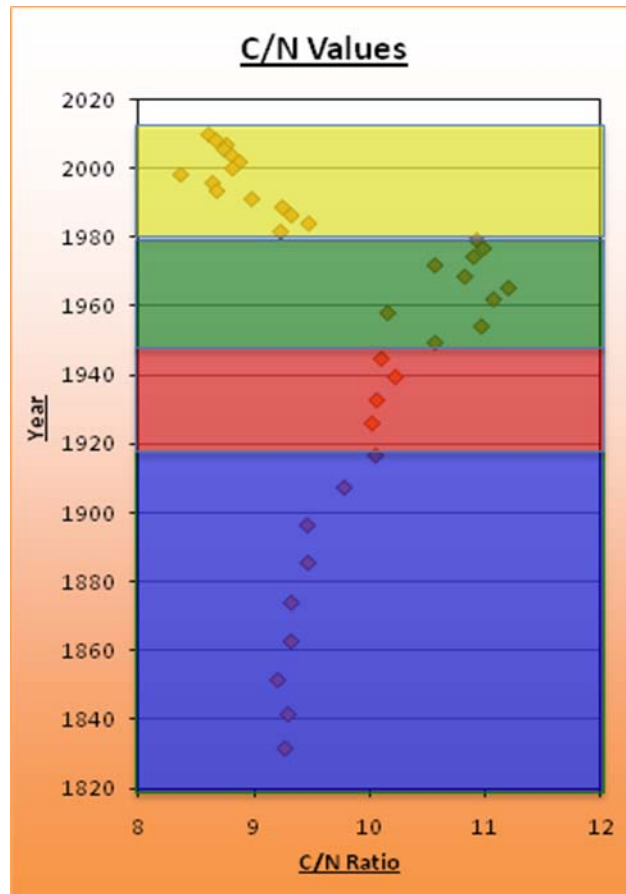


Figure 6: C/N Ratios

The phosphorus graph seen below has a very similar pattern to the carbon and nitrogen graphs seen above in figure 7. The blue represents when there was very little growth of the surrounding area. The red section shows when steady growth of the area began and we can see an increase in phosphorus accumulation. In 1831 we had a measurement of .214 ug/cm²yr and in 1982 it increased to 1.447 ug/cm²yr that is nearly a seven times increase. The green section below represents the farm crisis era and you can see a much lower intensity decrease of phosphorus accumulation, I believe that this is due to phosphorus recycling within the water column showing a much more gradual decrease in accumulation rates. After

development begins to boost again after the 1990's we see the accumulation rates shoot up to a new high and reaches 1.886 ug/cm²yr in 2007 this also supports the previous hypothesis that there was a excessively high amount of phosphorus in the lake during this time creating large algal blooms that disguise the increase of terrestrial input after the 1990's in the C/N graph.

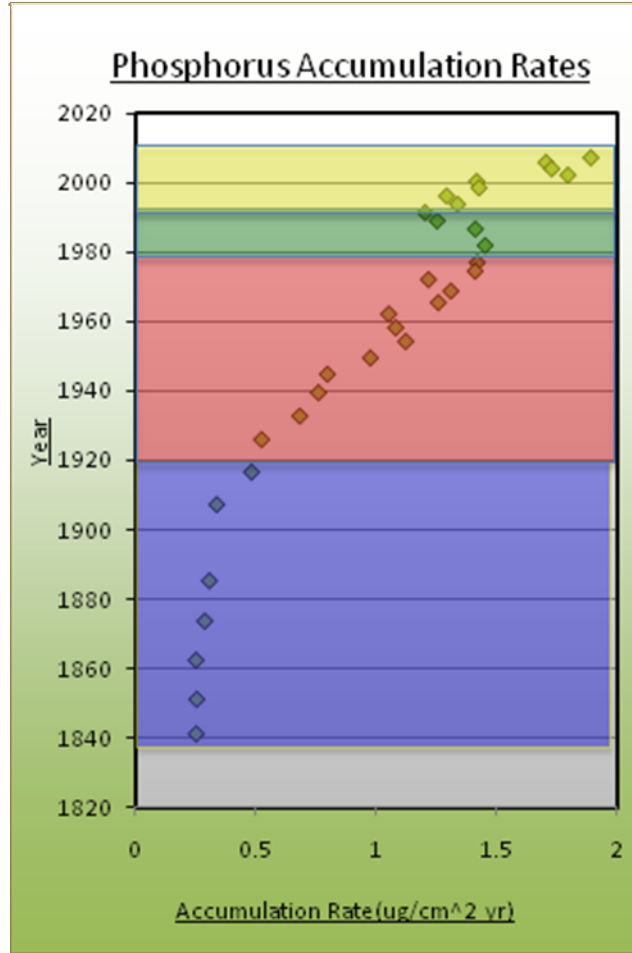


Figure 7: Phosphorus Accumulation Graph

From analyzing the samples on the ICP-AES I found that heavy metal accumulation rates varied closely to the previous stated graphs. The green represents when there was little growth in the area and rates were staying constant because of little anthropogenic pollution. We can see a steady growth in accumulation rates as people began to settle in the area which is represented by the blue section, rates increase by over five times. The yellow section shows the farm crisis era. As you can see there is a dramatic decrease in accumulation rates during the ten years that this era spanned. After the economy started to stabilize and development of the area started to increase there is an increase in rates of accumulation which is representative with the red shadowing. Arsenic is the only heavy metal that seems to not have a distinctive increase in accumulation rates after 1990. One hypothesis that I made based on this graph was because of the characteristic traits that arsenic has a similar chemical composition as phosphate. AsO_4 can commonly replace PO_4 in

plant growth which could be one reason why there isn't a significant increase in arsenic accumulation rates after the 1990's. In figure 8 you can see the maximum, minimum and average concentrations; these values show no significant health hazards and are well under sediment standards shown in table 1. [7]

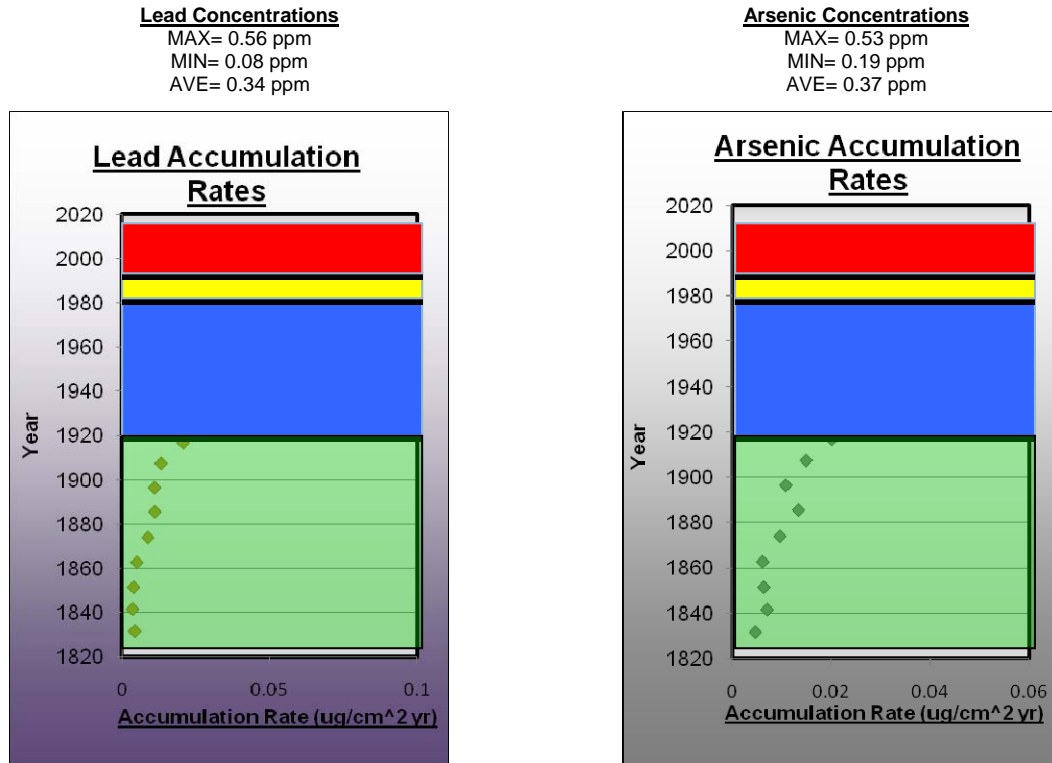


Figure 8: Heavy Metal Accumulation Rates

<u>Element</u>	<u>Effects Range-Low</u>	<u>Effects Range-Median</u>
Lead	46.7	218
Arsenic	8.2	70

Table 1: Sediment Standards for Elements of Interest

Conclusion

The results indicate that human activities have had a direct impact on the accumulation rates of the minerals and heavy metals depositing in sediments throughout history. Phosphorus, the element of interest, went up more than eight times from 1820 to present day showing a significant decrease from human settlement and development. These results also show that remediation efforts had no direct influence in the deposition of phosphorus burial in the sediment record. One possible hypothesis to why we see this unexpected result is because of phosphorus' ability to recycle within the water column annually by disturbance of

sediments or decay of plant material. Currently the watershed is focusing on reducing the amount of recycled phosphorus by removal of benthivorous fish and the removal of an invasive species, curlyleaf pondweed to target there excessive phosphorus problem.

Sources

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