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Anthropogenic Impacts as Revealed from Sediment Cores from Punderson Lake Ohio

Ronald A. Van Blarcum
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ANTHROPOGENIC IMPACTS AS REVEALED FROM SEDIMENT CORES FROM PUNDERSON LAKE OHIO

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ANTHROPOGENTIC IMPACTS AS REVEALED FROM SEDIMENT CORES FROM PUNDERS ON LAKE, OHIO

RONALD A. VAN BLARCUM

ABSTRACT
Sediment core archives provide a history of data useful for serving as a long-term monitoring reserve to evaluate chronological events of contamination to lake systems. This could be an effective tool for continual environmental management, monitoring and potential restoration efforts. This method is also very cost-effective without the addition of a water quality monitoring station on site. Taking 3 sediment cores from Punderson Lake Ohio for analysis has allowed associating variations in select metals to anthropogenic events or activities; we can determine a time frame with limited uncertainty and resolve the intensity of anthropogenic contamination to the lake starting with post World War II contamination till the present. We used sedimentation rate in conjunction with radiometric dating methods of 137Cs to establish a timeline through the cores. Applying mass depth g/cm² (Matisoff and Whiting, 2011) and core segmentation intervals (1cm) we can remove issue of porosity and compaction. Selected trace elements (As, Cu, Mn and Pb) were studied in these sediment cores. We can parse natural crustal sources of sediment input from anthropogenic sources using a method known as enrichment factor (EF) (Feng et al., 2004). This method requires the normalization of trace metal concentration against Al into an index/dimensionless data form (Essien et al. 2009). EF index implies a severity of contamination in a sediment interval allowing for the consideration of environmental impact, status of pollution and possibly source the contamination of the select trace metal. We can then plot EF over time to obtain relative burial times of the excess trace metals. We can then make a comparison to other regional lakes to see how anthropogenic source contamination appears in other systems. We used
diatoms as a biological component as they are sensitive to ecosystem/environmental changes and preserve well in buried sediment. Therefore, diatoms can be seen as responding to possible human influences that are changing the habitat or quality of the lake. We found correlations within the core showing trace element pollution related to anthropogenic activities. Primarily we can see strong signals of Pb and As in earlier portions of the core indicative of industrialization and fossil fuel burning of the time. We also see a rise in Cu enrichment at the top of the core which, is linked to CuSO₄ additions to the lake. Diatoms confirm that the CuSO₄ is having an impact on biotic components of the lake particularly changing their community structures. It is important to consider the benefits of this type of study. Future benefits such as building and periodically updating a data base that can be used to track a lake systems contamination levels and provide invaluable insight into remediation and site maintenance efforts.
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Chapter I

Introduction

Human modifications and changes to the planet continue to have an impact on ecosystems globally and locally. Our impact on a system is traceable through elements moving or added to a system by human means. One way to investigate anthropogenic effects on a system is to look at a sediment core (Kanfoush, 2013; Stephens et al., 2012). Sediment core archives provide a history of data useful for serving as a long-term monitoring reserve to evaluate chronological events of contamination to lake systems. High sedimentation rates in small lakes allow a cumulative sediment record to develop, establishing a timeframe of specific signal events that occurred in the lake (Adrian et al., 2009). Lakes rapidly show indications of environmental changes, meaning they have an accelerated response rate to the effects of the surrounding systems and often store these records in the sediment and organisms that reside there in (Hasbargen, 1994). Lakes respond faster than most terrestrial environments to changes such as, loss of trophic structure, pollution by metals or organic material, sediment load and seasonal variability (Peck et al., 2007). Therefore; lacustrine sediment analysis can provide data on trace metal contamination and diatom assemblage changes (Adrian et al., 2009). Understanding the anthropogenic effects upon surrounding systems near the lake can also
influence the lake itself (Rosenmeier et al., 2002) with clear cutting, burning, home construction, dam building and agriculture all influencing the material that is deposited on the lake bottom.

Many studies have been conducted on the process and impact on the Great Lakes however; we know less about the impact on small lakes that contribute inputs to the Cuyahoga River. Small lake systems provide input to a watershed along with pollutants and nutrients, or can act as a reservoir buffering a system from input by retaining material internally (Sanderson, 1987). Plenty of studies of larger lake systems have provided confounding information showing variations in data collected over the years, particularly from the Great Lakes (Pirrone and Keeler, 1996; Szalinska et al., 2011). Small lakes however, are mostly uniform in their depositional, hydrologic inputs and biological processes (Bookman et al., 2010).

We can then make a comparison to other regional lakes to see how anthropogenic source contamination appears in other systems (Gewurtz et al., 2008). Benefits of this type of study extend to not only the ecosystem but, also to the individuals that may be affected by changes to these systems and could be an effective tool for continual environmental management, monitoring and potential restoration efforts (Forstner, 2004). Providing historic and current data to an environmental management team can help elucidate the issues an ecosystem may be experience from early causes through changes in the system to the modern era (Pirrone and Keeler, 1996). This study will help elucidate the value of lakes within a watershed as indicators of anthropogenic changes. Punderson Lake was chosen as it has a well-documented history of human activities around and on the lake, the lake is in a position to receive weather patterns that could carry particulate
matter from Cleveland / Akron area to it and because it is the deepest kettle lake in Northeast Ohio. Lacustrine core analysis methods are cost-effective, as it integrates water quality information over time (Feng et al., 2004).

Several methods have been employed to determine the modern changes of Lake Punderson which can serve as a proxy for other similar lakes in the area (Hasbargen, 1994). We need to understand certain factors concerning the lacustrine environment to gain a comprehensive understanding of the core those are; deposition rate of sediments, concentrations of trace metals, depth of time in the core and biological process that have affected the core and are a part of the history. The use of multiple elements allows for a broader scope of indicators that should overlap and detail events through time down core (Forstner, 2004). This is due to the nature of each element having distinctive effects and interactions in the environment.

Deposition rates are important for calculating fluxes to the system instead of using concentrations, it is critical for the understanding of how elemental metals get into the aquatic system and are deposited in the sediment (Garcia et al., 2009). Sediment loads can also vary according to climatic events such as dry/wet seasons or years (Kanfoush, 2013). Using sedimentation rates we can establish a clear time of burial of each layer in the core (Osleger et al., 2008; Parsons et al., 2010). We know sedimentation rates in small lakes are usually higher than larger deeper lakes (Ontiveros-Cuadras et al., 2014). The uniform nature of sediment deposition increases temporal resolution through the core.

Sediment cores taken from Punderson Lake in northeast Ohio were analyzed for many trace metals, four were selected (As, Cu, Mn and Pb) as they are often associated
with known anthropogenic events or activities. Trace amounts of metals are common in all sediments around the globe but, elevated concentration can cause serious damage to flora, fauna and the ecosystem as a whole (Mann et al., 2013; Zhang and Liu, 2002). Human activities such as construction, energy production, automobiles and industrialization should have identifiable signals in the archive of lake sediments with increases in a concentration level shown in the sediment. A multi-heavy metals analysis down core can provide information about the influx of anthropogenic material into the lake system (Beolchini et al., 2013).

For our purposes 4 trace elements As, Cu, Mn and Pb were chosen for analysis, with several other elements acting as background variables (Al, Fe and Cr). Each element was chosen for study based on properties that can show variation through the core and are traceable with a possible anthropogenic source (Ontiveros-Cuadras et al., 2014). Lead is the most studied of my selected trace metals due in part to its natural toxicity in moderate levels in the environment. Lead (Pb), is a well-known hazardous element and has grown in abundance in the human made environment. Pb has been mined and utilized by humans for hundreds of years. In modern times since the industrial revolution (1850 to present) coined the Anthropocene (Crutzen and Steffen, 2003) considerable amounts of excess Pb were produced and added to the environment from fossil fuel burning (particularly gasoline), paint additives, piping, solder and ceramics. Pb in concentration can cause a variety of illnesses and damage to living organisms. In humans particularly Pb causes neurological disorders, reduction in higher brain functions and potential death. Natural concentrations of Pb occur in the soils globally close to 50ppm (Chaney et al., 1984) but, due to heavy industry and population growth these
numbers can reach and exceed 11,000 ppm (Gough et al., 1988). Pb can travel as a solute in water particularly in acidic conditions or as particulate in air. A source of excess Pb can be traced to leaded gasoline which was used since the 1930’s to prevent knocking in the automobile engine. Pb was first reduced by the enacting of the Clean Air Act of 1970, then from the removal in paint in 1972. Pb was further reduced as concentrations in gasoline were restricted in 1985 and completely removed by 1995 (Newell and Rogers, 2003). In 1988 the EPA limited the amount of Pb in drinking water to 15 µg/L and 0.15 µg/m³ as an air born particulate (EPA, 2001a; EPA, 2014). The US-EPA has found that Pb in particular has undergone an overall decrease in concentration in sediments since policies were enacted to reduce Pb inputs. The EPA’s data shows a continuing trend of decreased Pb through remediation and improvement in regulations that govern emissions (EPA, 2014). Pb is often transported into the lake via particulates; implying greater atmospheric deposition into a lake systems (EPA, 2006). The primary source of this atmospheric transport is the burning of fossil fuels. Thus a more homogeneous pattern of distribution would be expected as prevailing winds would deposit Pb and other trace metals over an area with consistency. There is considerable data variability from study to study involving Pb and could be related to core location, processing, ecosystem dynamics and other constraints.

Arsenic (As), like Pb has been a serious concern in the environment for years and remediation efforts have been targeted at reducing the modern concentrations in sediments and water (Painter et al., 2001). A major reason is that As is poisonous to most organisms even in small amounts. However, it is found naturally in almost all rocks in the environment as a trace metal but can also be found as arsenopyrite (AsFeS) associated
with iron mining, in coals or as a loose anion. Arsenic comes from several key sources as a pollutant, metal forging or smelting, fossil fuel burning (EPA, 2002). Concentrations easily bio-accumulate in flora and fauna. Arsenic is easily transported by water as an anion which is different from most other metals which form cations this can make it highly accessible and ubiquitous in the environment (Singh et al., 2007). The US-EPA has a standard for levels in water supplies of <10µg/L (includes automobile combustion) and use in various pesticides/rat poisons/herbicides (EPA, 2001b).

Copper (Cu) is another ubiquitous element that can be harmful in excessive levels in the environment. Copper is commonly included in most metal analysis papers as it is often in moderate concentrations in sediments near industrialized areas. The US-EPA has determined that 1.3 mg/L of Cu in drinking water is the limit for safety in the United States. Copper naturally occurs in water systems in levels equal to ~10ppb. Natural Cu is prevalent in crustal materials and heavily mined for use by people. Many human made items contain amounts of Cu including, homes, electronics, automobiles and money. Cu is also commonly used in fertilizers and pesticides/herbicides. Cu is transported as a dissolved solid in water and forms bonds with organic and inorganic sediment grains readily (ATSDR, 2004). Over 640 million kilograms were released into the environment as aerosol (air), particulate (soil, water and air) and as larger solids (soil) by industry alone in 2000 (EPA, 2008). Concentrations of Cu were found to be as high as 164ppm in the western basin of Lake Erie and up to 286ppm in Lake Ontario (Marvin et al., 2007). Cu pollution can come from groundwater contamination or from aerial transport and gravity deposition. Elemental Cu once in the environment does not break down but accumulates in soils, flora and fauna rapidly. As a cation it easily bonds to particulate
organic matter or to sediments. Few studies have researched copper and its potential impact on the environment particularly plants, algae or diatoms (van Hullebusch et al., 2003). Copper sulfate is a commonly used algaecide for control of algal blooms (Bookman et al., 2010) and is considered one of the most ubiquitous treatments for many smaller lakes and reservoirs (van Hullebusch et al., 2003) or in areas heavily used by people such as docks, beaches and marinas. The most common method of copper sulfate application is as CuSO₄+5H₂O which can come in several forms (powder or solid crystal) and quickly dissolves in aquatic systems (EPA, 2008). Copper is quickly absorbed by plants inhibiting photosynthesis (Korosi and Smol, 2012); it has a natural affinity for bonding as a particulate to organic matter and benthic sediment where it is then stored (Bookman et al., 2010). We know CuSO₄ is used as an algaecide in Punderson Lake. A signal should be evident from Cu trace metal analysis if the copper is accumulating rapidly in the sediments. We could also see potentially harmful side effects on the biotic communities from Cu poisoning in the waters.

Manganese (Mn) is a very common metal accounting for 0.1% of total Earth’s crust. Mn comes from a variety of sources mostly as a component in minerals such as rhodochrosite and pyrolucite but, can also be found in abundance as a cation with clays (Chukhrov et al., 1980). However, Mn is rarely studied as a pollutant. The global mean concentrations Mn in uncontaminated water systems is ~200µg/L (Howe et al., 2004). Mn naturally occurs as an aerosol from ocean spray, volcanoes and forest fires; otherwise it occurs as a dissolved or particulate solid in sediments particularly in reduction environments. The several anthropogenic sources of manganese to the environment include; wastewater discharges, sewage sludge, mining (particularly nickel ores) and
processing, emissions from different steel and alloys and fossil fuel combustion (including automobile, coal fire and natural gas) (Howe et al., 2004). Manganese is easily remobilized under reduction conditions; this can allow it to move in a system particularly where water is capable of transporting it as a cation (Lewis and Luther Iii, 2000; Li et al., 1969).

Implications arise that a large amount of other trace elements could find their way into a water system via atmospheric transport, ground water inputs or terrestrial run-off (Zhang and Liu, 2002). Each selected metal has an impact on the environment varying by accumulation and by toxicity level. Trace amounts of metals are common in all sediments but, elevated concentrations can cause serious damage to flora, fauna and the ecosystem as a whole (Ontiveros-Cuadras et al., 2014). Further we know that considerable variation exists in aerosol transport and deposition and that consistency in pattern is unlikely (Baltrenaite et al., 2014). These contradictions imply we do not fully understand the systems at work and hence more research is required. Examining anthropogenic impacts on small lake systems is not new. Studies have been conducted on a variety of lakes in regions all over the world. The impacts on these systems are often different but the systemic reasons for the pollution are usually closely related, as human generated pollution in the modern age has accumulated rapidly in systems globally (Hou et al., 2013).

We also determined a time frame with limited uncertainty to resolve the intensity of anthropogenic contamination to the lake at 40cm (~1950’s) to the present using $^{137}$Cs activity in the sediments. Finally we examined the sediment for biological components particularly diatoms as they are good bio-indicators of changes within an aquatic system.
Impacts on the diatom community are investigated in this study as diatoms are powerful biological tools and indicators of lake systems health and bio activity. Diatom assemblages respond to changes in nutrient level, macrophyte vegetation (Vermaire et al., 2012), water clarity and pollution (Anderson et al., 2012). Diatoms within a core can also show the periods when anthropogenic effects become more predominate as assemblages change with pre to post human occupation (Jiang et al., 2014; Wilson and Devlin, 2013). Diatoms respond quickly to changes in a system, population changes should reflect these changes in the lake such as acidification, eutrophication and pollution level changes (Anderson et al., 2012; Stevenson et al., 2013). Changes in these assemblages can easily indicate another time marker for confirmation of an anthropogenic effect on the system (Wolin and MacKeigan, 2005). Diatoms are primary producers and the collapse of their numbers can lead to unforeseen change in diatom distribution or worse a trophic cascade (Liu et al., 2013).

Studying the select metals and the diatom assemblages has formed a picture of the human impacts on the lake through time. The primary aim of this thesis will be to measure metal pollution in lake sediments and evaluate their potential impact at Punderson Lake Ohio. The secondary aim of this thesis is to evaluate the anthropogenic metal contamination in Punderson Lake for ecological damage and public health and safety.
Chapter II

Natural and manmade settings

2.1 Natural History of Punderson Lake Ohio

Punderson Lake is located at latitude 41° 27’12.74”N, longitude 81° 12’21.68”W.

Punderson Lake sits atop the glacial plateau that was formed from the last glacial period to cover part of Northeast Ohio during the Wisconsin Glaciation period, approximately 12,000 years ago at an elevation of 357 meters above sea level. Punderson is a kettle lake which, formed from large masses of glacial ice which ground down the surrounding land and provided overburden to depress the area where the lake now sits. Called a kettle lake because the large masses of ice left behind which form bowls or “kettles”; melted in place to fill the depressions.

It was during the Wisconsin glaciation period, the glacier carved out sections of the Cuyahoga sandstone-shale and Chagrin shale formations which are primarily Mississippian in age (Coogan, 1996) and then deposited significant glacial till a top those formations as it retreated. Punderson Lake began to form and was initially three small kettle lakes that became connected by small channels to form the larger lake we see today.
The lake resides at the bottom of a sloping hill that runs almost North to South, flanking the complete West side of the lake. The slope of the hill is gradual in some areas and steeper in others with anywhere from a 6% to 25%+ slopes (see Fig 1)(USGS, 1983). To the South and East the lake is abutted by a modern paved road and steep hill sides similar to the West flank. The North end of the lake is lower elevation land that contains a marsh. Soils around the lake are characterized primarily as Udorthents (Ud) which, are often of loamy material used for cut and fill and most of the soil is greater than 1.5 meters till bedrock along the high slopes (Deitrich et al., 2008).

Most of the soils around Punderson are considered well drained with the exception of some areas that are considered wetlands which are very poorly drained, particularly the marsh area to the North of the lake that are labeled as members of the Wellkill (Wc) soil profile type. Initial permeability of the land around the lake is considered slow mostly due to man-made interferences such as lawn grasses, pavement and compacted soil from construction and human traffic. The south end of the lake

Figure 1. United State Geological Survey Topographic map of the Punderson Lake area. Chagrin Falls Quadrangle 15’ (USGS, 1983)
formed an outflow that drains into the Bridge Creek tributary of the much larger Cuyahoga river system drainage basin. The lake is situated in an area commonly referred to as the “snow belt” and receives a considerable amount of snow and rain precipitation (Schmidlin, 1989).

Wind rose data from the National Resource Conservation Service can be used to indicate primary directions of wind flow and speeds across an area. Cleveland was first selected location as the source of atmospheric pollution that could be carried to the lake. Cleveland Wind Rose data was collected over a 30 year period and averaged on a circular plot indicating frequency of wind blows from a cardinal direction. The intensity is gauged by color and centered at the gauge location. For most of every month wind direction comes primarily from the Southwest / West Southwest direction. Punderson Lake is almost directly East of Cleveland. This could imply that most of the atmospheric material carried on winds leaving Cleveland would not likely cross directly over Punderson Lake. However, when Wind Rose data for Akron Ohio was looked at, the wind pattern pushes almost directly over Punderson which is Northeast of Akron. The winds from Akron blow in the strongest and most frequently from the Southwest, West Southwest and West. In Fig 2 four months (March, June, September and December), 30 year averaged wind rose plots from Akron Ohio show the intensity and frequency of wind direction. The average wind speed was measured between 3.78 and 5.15 m/s.
Figure 2. National Resource Conservation Service, Wind Rose data Akron, Ohio 1960-1990. (NRCS, 1996)
Precipitation events are a major input into the Punderson Lake system which, also receives some spring fed groundwater flow and drainage from a nearby wetland. Average precipitation for the year (2012) excluding snowfall over Lake Punderson was 50.2 cm (see Fig 3). The average snow-fall between December 2012 and February of 2012 was approximately 74.1 cm (MRCC, 2014). Temperatures range from cold winters averaging -4°C to warm summers with an average of 21°C with annual averages near 10.5°C in 2013 (MRCC, 2014)(see Fig 4).

**Figure 3.** Average annual precipitation in the Lake Punderson area. Does not include snowfall (National Weather Service, 2014).

**Figure 4.** Annual mean temperatures in the Lake Punderson area (National Weather Service, 2014).
Due to the changing seasons the lake waters undergo seasonal turn-over from water temperature changes and density variations. During warming in spring the lake will begin to turn-over as surface waters warm and ice melts. The warm waters will begin to form convection currents in the epilimnion circulating nutrients upwards from the hypolimnion and providing food resources to plankton and algae. During the fall this turn-over event happens again, this time as water cools and becomes more dense sinking to the bottom taking nutrients and food resources with it. This turn-over cycle is important for the lakes biotic community. In Punderson turn-over can take up to a month as some portions of the lake are deeper than others. During Fall and Spring stratification the lake likely experiences some bottom hypoxia. Bathymetric data indicates the average depth of Lake Punderson is approximately 10 meters with a believed deepest point of 20 meters in the central basin. The location puts the lake in the pathway of winds that pass over Lake Erie and Western Ohio allowing precipitant and airborne material to be potentially deposited over Punderson Lake.

2.2 Human History of Punderson Lake Ohio
The historical use and human history around the lake is well documented from the Ohio department of natural resources. The park and lake are named after Lemuel Punderson the first person to permanently settle in the area in 1808. Originally Mr. Punderson constructed a dam at the south end of the lake to power a small mill; he also built a home that is no longer standing near the lakes edge. W.B. Cleveland saw an opportunity to acquire the land and lake in the early 1900’s and in 1904 constructed a home where the current manor house resides. The lake and property were called Lakeside farms and used as a privately operated hunting and fishing reserve. Eventually the lake became a place for wealthy Clevelanders and other locals to visit to escape the city. In 1929 the land was
owned by Karl Long who could not financially support the property. The population of the area was growing and some homes and roads were built around the property during this time. Investors in the property began construction on a Tudor style manor house in 1929 however; the house was not completed until 1948.

In 1948 upon the completion of the manor house the Ohio Department of Natural Resources (ODNR) Wildlife Division acquired the land around the lake (~850 acres) and the lake (~100 acres) for the purposes of hunting and fishing. In 1951, the whole land resource was transferred to the Division of Parks and Recreation and converted into a park. The ODNR Parks service renovated and opened to the public the manor house in 1956 to serve as lodging for guests. Another structural renovation of the park was completed in 1982 which added further amenities for guests including small cabin lodges, an updated marina area, a beach and recreation area (ODNR, 2008).

![Figure 5. Population of Newbury Ohio.](US Census Bureau, 2010)

Expansion of homes and industry around the lake and park area have potentially increased run-off as population increases in the area rose considerably between 1950 and 1980 (see Fig 5). The run-off may include more sediment, pollutants (such as fertilizer, heavy metals and petroleum products) and sewage from leaking septic systems. The EPA
has determined that there is a relatively high index of groundwater pollution potential in
the area surrounding Lake Punderson due to hydrology and human use (Deitrich et al.,
2008). The park service of the ODNR in 2005 began a beautification of the lake project
which required the addition of herbicides to the lake to kill littoral vegetation and reduce
the risk of algal blooms. Each season they spray areas to control growth particularly
around the docks, the beach and the marina.
Chapter III

Methods

3.1 Sampling methods

Sediment core extraction was done using a 45cm gravity coring device. We extracted 5 cores from the lake bottom at water depths averaging 10 meters. One core was taken during the winter of 2013 the other 4 taken during the summer of 2013. Locations for each core were taken and recorded via GPS and plotted on a map as seen in Appendix Fig. 1-2 and below on Table 1.

<table>
<thead>
<tr>
<th>Core #</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth (m)</th>
<th>Core length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL-2</td>
<td>N 41° 27' 09.5&quot;</td>
<td>W 81° 12' 49.1&quot;</td>
<td>10</td>
<td>39</td>
</tr>
<tr>
<td>PL-3</td>
<td>N 41° 27' 19.5&quot;</td>
<td>W 81° 12' 21.27&quot;</td>
<td>10</td>
<td>38</td>
</tr>
<tr>
<td>PL-4</td>
<td>N 41° 27' 26.54&quot;</td>
<td>W 81° 12' 32.24&quot;</td>
<td>9.5</td>
<td>32</td>
</tr>
<tr>
<td>PL-5</td>
<td>N 41° 27' 33.74&quot;</td>
<td>W 81° 12' 33.26&quot;</td>
<td>10</td>
<td>45</td>
</tr>
</tbody>
</table>

Attempts were made to ensure consistency of each core by staying at relatively the same depth and length of each core. Core 1 and 3 could not be processed for this study due to time constraints therefore, only cores 2, 4 and 5 will be used. The average sediment core
was 39cm in length and processed by sectioning 1cm increments of sediments into 50ml laboratory tubes. 1cm segments from each core were then processed in the lab to extract water for sample drying. Each tube was weighed before and after water extraction. Samples from cores 2, 4 and 5 were then completely dried in an oven at 50°C. Dry weights were then taken of each sample and recorded. All samples were measured for bulk density by calculating the cross-sectional area of each tube (cm²) and dividing by dry weight (g). Sample sediments from both cores 2 and 5 were then homogenized by pulverization in a mortar and pestle and weighed again to verify that no significant amount of material was lost during the homogenizing process.

Samples from core 5 were then sent to Case Western Reserve University for radiometric ¹³⁷Cs dating and sedimentation rate calculations. Samples from core 2 were sent to the Northeastern Ohio sewer districts labs for metal testing. Core 4 was processed for diatom analysis. Cores were similarly weighed, dried and washed to remove all lose sediment so only diatoms remained to be counted. Sediments in each core were also examined for primary sediment structure.

3.2 Radiometric Dating Method
Radiometric dating was conducted by Dr. Gerald Matisoff’s laboratory at Case Western Reserve University using a High Purity Germanium Detector (HPGe) system. Sediment samples we analyzed by a HPGe system was used to determine the activity peak for ¹³⁷Cs (661.62 keV). Once activities were established we used the following model called the “mass sedimentation rate model” to determine a sedimentation rate using the depth of the ¹³⁷Cs maximum activity (Boniwell, et. al, 1999). With this model we use mass depths (g/cm²) instead of linear depths to correct for porosity and compaction in buried sediment.
\[ \Phi / A' / T_1 - T_0 \] \text{ Eq 1.} \\
Cum dry wt (g) [\Phi] / cross sec core (cm^2)[A'] / sample year [T_1]– \(^{137}\text{Cs}\) peak yr [T_0].
Cumulative dry weight above the \(^{137}\text{Cs}\) peak ing grams / core cross sectional area in cm^2 / year core taken minus 1963 (maximum \(^{137}\text{Cs}\) fallout).
\[ \text{Md} / (T_1 - T_0) \] \text{ Eq 2.}
Mass Sedimentation Rate (MSR) where Md is the mass depth in the core of the maximum \(^{137}\text{Cs}\) peak, \(T_1\) is the current year and \(T_0\) the year of peak \(^{137}\text{Cs}\) atmospheric fall-out determined to be 1963 (Matisoff and Whiting, 2012) from related \(^{90}\text{Sr}\) data. In this model the mass sedimentation rate is assumed to be constant throughout the sampling interval. Since we have a mass depth in core, a sedimentation rate and a peak year of \(^{137}\text{Cs}\) fall-out we can determine an approximate age of each cm of core. \(^{137}\text{Cs}\) radiogenic date (Kanfoush, 2013) can be used to give time scales to a sediment core and also provide sediment deposition rates (Kirchner, 2011; O'Reilly et al., 2011). From atomic weapon testing, atmospheric \(^{137}\text{Cs}\) signal is at a peak in 1963, establishing an effective marker within the sediment record of Punderson Lake (Cutshall et al., 1983).

### 3.3 Metal Analysis Method
All samples from core 2 were processed by homogenization and sent to the Northeast Ohio Regional Sewer District (NEORSD) lab for analysis on ICP Spectrometer. Before samples could be run on the spectrometer they need to be digested in a microwave system to extract metal ions. NEORSD uses an internal method microwave digestion called 3051A which mimics EPA method 200.2. Set up for digestion requires Teflon microwave safe digestion vessels. Dry homogenized samples from each centimeter of the core were taken in approximately 0.1 grams and placed into a clean Teflon vessel. 8 mL of HNO₃
(concentrated 16M) and 2mL of HCL (concentrated 12M) were added to each vessel. Vessels were capped and placed in the microwave and digested at 175±5 C° for 20 minutes. Once digestion is complete the samples are removed to cool and the remaining sample will be the injection fluid for the ICP. Samples injected into the ICP were continuously calibrated with the Sewer District’s internal standards to insure quality control. The NEORSD has strict quality control measures due to the nature of their business as a provider of clean water and public health safety. They therefore must comply with all governmental regulations (State and Federal) regarding laboratory methods and testing restrictions. The Sewer District provided both raw and calibration corrected data to me for retention and inspection as a final quality control measure (see Table 2)

Table 2. Sample mean and standard deviation of selected trace metals reported in ppm, with laboratory recovery mean and standard deviation and percentage recovery.

<table>
<thead>
<tr>
<th>Punderson</th>
<th>As</th>
<th>Cu</th>
<th>Mn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core #2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean sample</td>
<td>26.55</td>
<td>95.86</td>
<td>1581.85</td>
<td>118.73</td>
</tr>
<tr>
<td>± sd</td>
<td>±6.58</td>
<td>±24.09</td>
<td>±529.34</td>
<td>±45.93</td>
</tr>
<tr>
<td>mean recovery</td>
<td>1975.91</td>
<td>1924.09</td>
<td>1965.85</td>
<td>2071.49</td>
</tr>
<tr>
<td>±sd</td>
<td>±91.35</td>
<td>±94.57</td>
<td>±81.72</td>
<td>±98.04</td>
</tr>
<tr>
<td>Recovery %</td>
<td>101.1</td>
<td>81.5</td>
<td>130.96</td>
<td>96.5</td>
</tr>
</tbody>
</table>

3.4 Diatom Analysis Method

Samples were taken from the top 3cm, 10cm, 11cm and the bottom 1cm (32cm) from core 4. Sediment samples were prepared by taking 0.5g of sediment for each interval to be tested into separate beakers. Samples are soaked in 5mL of H₂O₂ (Hydrogen Peroxide) for 12 hours to break down the sediments and separate all the particulates in solution. 15mL of de-ionized water (DI) and 10mL of HNO₃ (Nitric Acid 60%) and allowed to boil on a hot plate till only 10ml of solution remained. This boils off
some of the HNO$_3$ and H$_2$O$_2$ first cleaning the solution and dissolving away all organic particulates. Solutions are rinsed 5 times every 5 hours with DI water to clean diatoms for mounting on a slide. Slides were then prepared with cover slips and slowly evaporating remaining fluids from samples onto slides. Slides are then mounted using Naphrax adhesive. Each slide is examined for diatoms under a light microscope on 100x power and lens oil. All diatoms are counted by valve and sorted into genera and species if determinable.
Chapter IV

Results

4.1 Radiometric Dating

All sediment cores taken were similar in depth, length and sediment makeup. Sediments consisted primarily of clays and silts with interspersed sand. At the top of each core sediments were less compact and contained more organic matter and more organic activity, such as worms. Compaction and reduced porosity became more apparent at approximately 20cm with clays heavily compacted at the bottom of the core. Cores showed little variation in color, changes in grain size or any evidence of lake bed modification such as dredging or dumping.

Figure 6 shows the results of $^{137}$Cs detection. An obvious peak appears 5.163 g/cm$^2$ (38 cm) down-core, this peak represents the max $^{137}$Cs fallout from atomic weapons testing in the atmosphere and can be assigned a determined date of 1963 (Matisoff and Whiting, 2012). This marker point is inferred from monthly atmospheric readings of $^{90}$Sr which is linked to $^{137}$Cs. Hence, we can use 5.163 g/cm$^2$ (38 cm) as our direct age marker in core and extrapolate other dates through the core using 1963 as our base making the bottom of core #5 ~1952 [2013-(6.34 g/cm$^2$/0.1033 g/cm$^2$/y)]$^{[1]}$. Confidence in $^{137}$Cs data is very high (see Fig 6) due to confirmed Cs fallout markers and monthly $^{90}$Sr data (Matisoff and Whiting, 2012). Sedimentation rates were approximately equal to rates obtained from bulk density measurements of cores from Lake Erie.
4.2 Sedimentation Rates
Sedimentation rates were determined by obtaining maximum mass depth (g/cm²) divided by year the core was taken back to our $^{137}$Cs peak. The formula below shows the calculation.

$$\text{Dry Mass sedimentation rate} = \frac{5.16276 \text{ g/cm}^2}{(2013 - 1963)y} = 0.1033 \frac{\text{g}}{\text{cm}^2 \text{y}}$$

The results of this sedimentation rate calculation account for porosity and compaction with the sediment core. The formula also assumes a consistent rate of sedimentation through time.
4.3 Trace Element Concentrations

Concentrations of metal ions in ppm in sediment cores reflect a sediment load input from several possible sources, terrestrial run-off or direct precipitation from rain events over lake waters (called surface inputs) and groundwater input. Excess metal concentrations reflect a variety of anthropogenic effects including: fossil fuel consumption, home construction/landscaping, pesticide/herbicide/fungicide applications, fertilizer, metals from cars/boats and other sources and road construction as a partial list. What we see is almost all the metals tested for followed the same general trend through the core with a few exceptions As, Cu, Mn and Pb. At the bottom of the core we see Levels rise and fall as they proceed up core, while some lines have sharper increases or decreases the general pattern remains between all the metals analyzed. Some trace metals are more indicative of human activity such as As, Cu, Mn and Pb. All 4 of these metals show distinctively different profiles downcore when compared to other metals such as Al or Fe (see Fig 7).
Figure 7. Concentrations of select trace metals in sediments from Punderson Lake, before conversion to Enrichment Factor, core #4.
Primary sources of sediment from run off contain mostly silica then high quantities of Fe and Al. Aluminum makes for a good base line to normalize to since the influx is tied to the rate of sedimentation and is in abundance throughout the core. Normalizing to Al is a technique that produces a dimensionless index for separating potential anthropogenic effects from natural terrestrial inputs. To calculate we need to determine the enrichment factor of the metal in question while removing the amounts that potentially came in with a stream of terrestrial natural sedimentary Al (Zhang and Liu, 2002).

\[
\frac{(TM_s / Al_s)}{(TM_s / Al_b)} \]  \text{Eq 3.}

Enrichment Factor (EF) (Zhang and Liu, 2002). Where TM = Target Metal, sample is our sample selection level and background = the preindustrial levels of the element in question TM/Al \text{[3]} (Xia et al., 2012(see Table 3). A table of the severity of contamination has been developed by (Essien et al., 2009) that applies the EF to an index of severity (see Table 6 in the Discussion section).

<table>
<thead>
<tr>
<th></th>
<th>EF Cu</th>
<th>EF Pb</th>
<th>EF Mn</th>
<th>EF As</th>
</tr>
</thead>
<tbody>
<tr>
<td>average</td>
<td>4.2385</td>
<td>2.1994</td>
<td>2.6776</td>
<td>3.8465</td>
</tr>
<tr>
<td>±sd</td>
<td>1.4300</td>
<td>2.7820</td>
<td>1.2061</td>
<td>0.9830</td>
</tr>
<tr>
<td>Minimum</td>
<td>2.2968</td>
<td>3.3422</td>
<td>1.2821</td>
<td>2.4175</td>
</tr>
<tr>
<td>Maximum</td>
<td>8.3171</td>
<td>13.2485</td>
<td>6.6814</td>
<td>6.3816</td>
</tr>
<tr>
<td>Depth of Max</td>
<td>1cm</td>
<td>27cm</td>
<td>1cm</td>
<td>27cm</td>
</tr>
</tbody>
</table>

In the case of normalizing to Aluminum we can equalize all results to a known estimated abundance of Al in the Earth’s crust (69,300ppm) (Guieu et al., 1997; Martin and Whitfield, 1983), or local background values if available in our case 23,000ppm (Yuan, 2013). Once Al background levels are known, the Enrichment Factor (EF) can be
calculated to determine the severity of metal contamination in the sediment layers (Essien et al., 2009; Feng et al., 2004). When plotted over time we now see when contaminates were buried in the sediment column.

Lake Erie Al ppm core sediment samples can be averaged with global Al ppm in sediments to get a background level (Yuan, 2013).

4.4 Diatom Analysis
Slides were analyzed from different levels of the core. We selected the bottom of the core (32cm) to identify past communities, sampled middle of the core at 10cm to see pre-copper sulfate assemblages and finally looked at the top of the core 3cm and 2cm for evidence of community changes among diatom genera and species (if identifiable). Slides showed considerable remaining particulates and grains of sand, silt and clay with clay being the most abundant in each slide. Top layers of the core had most diatoms relatively intact with some broken or unidentifiable pieces mixed throughout. Deeper layers of the core had significantly more broken or unidentifiable diatom pieces. Count totals for each level were set to a minimum of 400 valves. Each level of the core was analyzed using a Shannon’s Diversity Index (H’), Evenness score (E_H) and percent abundance by genus.

Table 4. Results of H’, E_H and most abundant genus found in 3 levels of core.

<table>
<thead>
<tr>
<th></th>
<th>Top (Post-CuSO_4)</th>
<th>Middle (Pre-CuSO_4)</th>
<th>Bottom (Pre-CuSO_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shannon's Diversity H'</td>
<td>2.482</td>
<td>2.533</td>
<td>2.378</td>
</tr>
<tr>
<td>Shannon's Evenness E_H</td>
<td>0.408</td>
<td>0.415</td>
<td>0.397</td>
</tr>
<tr>
<td>Most Abundant Genus</td>
<td>Stephanodiscus</td>
<td>Cocconeis</td>
<td>Puncticulata</td>
</tr>
</tbody>
</table>

Populations show relatively equal diversity between each level in the core and show equal evenness throughout the core as well. The diatom community makeup
however, changes considerably with dominant genus varying in each level of the core (see Fig 8).

**Figure 8.** Diatom percent abundance by genus in 3 levels of the core. Top 4,5,6cm, 16,17,18cm and bottom 40,39,38cm
Chapter V

Discussion

5.1 Comparison of Large Great Lakes to Punderson Lake

Anthropogenic inputs into a system can have immediate and long term effects. Understanding the relationship of these effects and the impacts on the aquatic system are important goals of lake quality assessment. Lake sediments retain an archival record of events that have occurred through time to the systems and accessing that record can provide a comprehensive history of anthropogenic manipulations to the system (Stephens et al., 2012). However, large lakes such as Lake Erie are too complex and dynamic to be considered in a single comprehensive study (Azcue et al., 1996). Compared to smaller shallower lake systems; it should be easier to assess a smaller system for the potential impacts that may have occurred over time due to uniformity of the system. Beyond size issues we must consider pollution transport and input vectors to a system as well (Ontiveros-Cuadras et al., 2014).

We must assume that each lake does not get an equivalent share of pollution from atmospheric transport and rainfall events (Trimble et al., 1999). With Cuyahoga County receiving a yearly average precipitation level less than neighboring East counties of Geauga and Lake (MRCC, 2014). We can therefore assume that the processes of atmospheric deposition and pollution distribution are interlinked and distributed over the area with regards to precipitation levels. We can also assume that while precipitation rates are variable year to year with wet and dry year intervals the overall average is proximal and as such the sedimentation rates connected to run-off events should also be
relatively constant in a smaller shallow lake particularly on this studies time scale. We also can assume that because Punderson is a “rural” lake the degree of the pollution would be less severe aka enrichment factors should not be at the highest levels.

Geochemical analysis of cores from the Great Lakes shows enrichment factors indicating a level of contamination caused by human activity. From my own research and test results a similar amount of contamination was also present in cores taken from Lake Punderson. Several case studies of different Great Lakes and with Lake Punderson were compared via correlation analysis. When a correlation analysis was performed using data from several other sources (Leland and Shimp, 1974 [Lake Michigan], Pirrone and Keeler, 1996 [Lake St. Clair], Gewurtz, et al., 2008 [Lake Huron and Superior], Yuan et al., 2013[Lake Erie] and this study; data from Punderson Lake 2013) it was found that among my selected elements of As, Cu, Mn and Pb there was a strong positive (+1) correlation. Each system appears to be receiving equivalent input of trace metals in abundance of natural baseline sources relative to the parameters of sedimentation, lake volume and pollution source points (see Table 5).

Table 5. Values are ratios of concentration in mg/kg divided by Al mg/kg. Lake Erie data from (Marvin, et al., 2007), Lake Michigan data from (Leland and Shimp, 1974) and Lakes Huron/Superior data from (Gewurtz, et al., 2008).

<table>
<thead>
<tr>
<th></th>
<th>Punderson</th>
<th>Erie West</th>
<th>Erie Cent</th>
<th>Erie East</th>
<th>Michigan</th>
<th>Huron</th>
<th>Superior</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.00063</td>
<td>0.00053</td>
<td>0.0006</td>
<td>0.00071</td>
<td>0.00041</td>
<td>0.000146</td>
<td>0.00013</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00229</td>
<td>0.00282</td>
<td>0.00266</td>
<td>0.00204</td>
<td>0.00124</td>
<td>0.000373</td>
<td>0.00155</td>
</tr>
<tr>
<td>Mn</td>
<td>0.03853</td>
<td>0.03916</td>
<td>0.04714</td>
<td>0.05692</td>
<td>0.02453</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Pb</td>
<td>0.00283</td>
<td>0.00344</td>
<td>0.00323</td>
<td>0.00192</td>
<td>0.00235</td>
<td>0.000443</td>
<td>0.00075</td>
</tr>
</tbody>
</table>

Lake Erie was divided into 3 basins for sediment core analysis because of the variability between each basins ecosystem dynamics. Lake Punderson sediments can be compared with Lake Erie sediments with respect to selected trace elemental concentrations.
Normalizing to Al was necessary to make the correlation between all the lake systems concentrations of metals and is averages of total contamination from sediment cores. Using Al normalization allows us to remove background sediment and see ppm of target metals. Several assumptions can be made from this data; distributions of selected metal pollution are relatively equivalent and increased enrichment factors imply heavier anthropogenic usage and system stress. Even though the watershed of Lake Erie is considerably larger the over flux input ratio of metals is close to the same as Punderson particularly in the West and Central basins. From our results we obtained sedimentation rates from Punderson lake, we wanted to compare these rates to Lake Erie. Cores taken from Lake Erie near the Western basin reveal that bulk density sedimentation rates are about equal to Punderson. The conclusion drawn from this is that over all Punderson sediments contained more overall water and organic material as Punderson is a eutrophic system. Elements in other lakes, Huron, Superior and Michigan all show distinctly different signatures relative to each trace metal. This is due to the extreme variations between all these lakes. Superior, Huron and Michigan are all much deeper and have different localized environments. This means we can draw a link between small lakes in the Erie watershed and Erie itself because these lakes share similar sediment inputs and constraints from the environment.

5.2 Potential impact and implications of lake pollution.
All the select metals can have an impact on the ecosystem health of Punderson Lake. Fortunately some remediation efforts are in place and working to remove some of the pollution from the environment. We know Pb and As are primarily atmospherically transported pollutants to Punderson. Pb begins at a lower baseline then rises to a considerable peak around 34cm (~1970’s) then begins a gradual decline 26cm (~ early
1980’s) then a sharp decline then dropping off to levels below that of 40cm (~1950) by 10cm (~2000’s). As follows an almost identical, though diminished version of the Pb line (see Fig 9). As starts with lower concentrations at 40-34cm (~1950’s – early 1960’s) rising after 10cm (~ 1970’s) then beginning a decline by 15cm (~1980’s -1990’s) eventually falling below initial sampled levels at 40cm.Cu initially follows a profile trend identical to other metals. Then begins a rise at 23cm (~mid 1990’s) but still following the profile of other metals though more elevated, then around 10cm (~2000’s) begins a significant climb much higher than previously seen. A similar effect is going on with Mn, much like Cu it starts with relatively low levels of concentration and begins a gradual increase then a sudden jump after 11cm. In order to be able to display all of these trace metals on a single graph we need to normalize them to an index (Enrichment Factors) and remove the ppm concentrations.

Both As and Pb are on the decline in the lake, though levels still indicate minor to moderate enrichment respectively. Possible sources of As and Pb contaminate are likely from atmospheric particulate carried over the region from a major urban area like Cleveland or Akron. Pb is a well know byproduct of fossil fuel burning and automobile usage, and As is also tied to fossil fuels and metal smelting both activities well connected to the Cleveland/Akron area. Arsenic is particularly dangerous as it mobilizes very quickly in water and is easily bio-accumulated in flora and fauna. Fortunately, As becomes less mobile once trapped in sediments unless under oxidizing conditions or acidic systems (Lamie, 2012)(see Fig 9). Punderson sediments are rich in clays with low porosity and have a more alkaline pH, remobilization of Arsenic from lower levels downcore where concentrations are higher is unlikely. Even with a decline in As in the
sediment there is still a minor enrichment $<3\times 1$ (see Fig 9) as concentrations are now at levels below those found at the bottom of the core (40cm).

Table 6. Enrichment factor severity index. (Essien et al., 2009)

<table>
<thead>
<tr>
<th>EF</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>No enrichment</td>
</tr>
<tr>
<td>&lt;3</td>
<td>Minor enrichment</td>
</tr>
<tr>
<td>3-5</td>
<td>Moderate enrichment</td>
</tr>
<tr>
<td>5-10</td>
<td>Moderately Severe enrichment</td>
</tr>
<tr>
<td>10-25</td>
<td>Severe enrichment</td>
</tr>
<tr>
<td>25-50</td>
<td>Very Severe enrichment</td>
</tr>
<tr>
<td>&gt;50</td>
<td>Extremely Severe enrichment</td>
</tr>
</tbody>
</table>
Figure 9. As, Cr, Cu, Mn and Pb converted to enrichment factors over time. EF displayed with 1σ deviation. Dates given are a calculated approximation (±2.5cm).
Pb shows moderate enrichment factors in the sediment but, these concentrations are still significantly less than 39-40cm (~1950’s levels (moderately severe, see Fig 9)) and dramatically less than the 35-25cm (~1960-1970s). The clear indication of atmospheric Pb transport and deposition is confirmed by the extremely high levels of contamination from the 1960s through the 1970s. As industrialization and populations were very high in Cleveland and Akron at those times and Pb in gasoline and from fossil fuel sources such as the downtown Cleveland coal fire plant were constantly polluting the local atmosphere. Atmospheric transport via weather patterns are the only way to explain such excessive levels found in downcore sediments. Removal of Pb from gasoline in the 1980s and 1990s is clearly visible on Fig. 9 (24-10cm) as well as remediation efforts driving down total concentrations were implemented in earnest. Pb can easily migrate up and down core through oxidation processes related to organic decomposition, especially in the presence of Fe and Mn exchange ions (Hou et al., 2013). This could have caused the problem seen with $^{210}$Pb dating as near surface decomposition of organic material allowed Pb to mobilize and migrate up core making dating with Pb difficult. However, in lower portions of the core Pb can become trapped within silicate matrixes of clay with ion exchange higher pH levels and lower porosity reduces further exchange potential (Scrudato and Estes, 1976).

For beautification purposes copper sulfate and other algaecides were added to several areas of Punderson Lake (namely the marina, the beach and dock areas) as a tracked program by the ODNR starting in 2005. Copper sulfate may have been added at previous dates but no records exist of this action by the ODNR. A clearly delineated increase is apparent in copper concentrations in the upper portions of the core from
Punderson Lake. The timing coincides with the ODNR project and addition of CuSO$_4$ to the lake (Mayo, 2014). However, at first glance many would argue that the amounts of Cu added to the system seem too low on average to increase the values so drastically in the core. We do see a rise in Cu ppm concentrations from 2006 till 2013, these additions could be indicative of the additional flux we observe in enrichment content (see Table 7). To confirm the values changing near the top of the core I compared direct amounts applied to amounts of change per cm in the core. To do this I simply used known percent pound values of Cu in each type of herbicide to the amount of gallons applied over the area and converted that to ppm. I use ppm because the values obtained from ICP analysis of the core are recorded in ppm as well.

\[
Cu \text{ (lb/gal)} \times 453.59/3.79 \text{ (g/kg)/1 (lb/gal)} \quad [4]
\]

\[
mg/kg= g\times 1/(mg) \quad [5]
\]

\[
A= \frac{ac}{40,468,564.2 \text{ cm}^2} \quad [6]
\]

\[
mg/kg / A \quad [7]
\]

A simple comparison table shows some interesting commonalities in the amount of Cu added via herbicide and the amount recorded from analysis (see Table 8).

Part of the Cu flux may be from other sources but, also from plant matter that absorbed the Cu that was added and then died settling on the bottom, got buried and added to the overall flux of Cu (see Fig 9). There is a signal that is seen from the addition of herbicide with some variations that could be other sources. It is also possible that the correct amounts of CuSO$_4$ were not applied and recorded hence we have some margin of error and uncertainty.
Table 7. Herbicide additions to Punderson Lake (Mayo, 2014).

<table>
<thead>
<tr>
<th>Type of Herbicide</th>
<th>Chemical make up</th>
<th>Year</th>
<th>Gallons</th>
<th>Acres</th>
<th>Cu(lb)/gal</th>
<th>mg/kg cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nautique</td>
<td>CuSO₄</td>
<td>2006</td>
<td>10.3</td>
<td>1.04</td>
<td>2.06</td>
<td>1.23</td>
</tr>
<tr>
<td>Cutrine Plus</td>
<td>CuO₂N₂H₆</td>
<td>2006</td>
<td>2.6</td>
<td>0</td>
<td>0.234</td>
<td></td>
</tr>
<tr>
<td>Nautique</td>
<td>CuSO₄</td>
<td>2007</td>
<td>22.6</td>
<td>1.82</td>
<td>4.52</td>
<td>2.4</td>
</tr>
<tr>
<td>Cutrine Plus</td>
<td>CuO₂N₂H₆</td>
<td>2008</td>
<td>8</td>
<td>0</td>
<td>0.72</td>
<td>.11</td>
</tr>
<tr>
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<td>2012</td>
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<tr>
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<td>2013</td>
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</table>

| | Totals | 353.5 | 66.24 | 95.87 | 30.04 |
| | Average | 22.09 | 4.14 | 5.99 | 3.76 |
| | gals/yr | 9.46 | 13.70 | 1.45 | |
| | Acr/yr | 2013 | 6.24 | 2013 | 5.00 |

Table 8. Comparison of calculated Cu mg/kg vs ICP analyzed Cu mg/kg

<table>
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<th>Depth</th>
<th>Additional Cu mg/kg</th>
<th>Cu mg/kg in core</th>
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<tr>
<td>cm 2</td>
<td>12.46</td>
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<td>cm 3</td>
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<tr>
<td>cm 4</td>
<td>5.83</td>
<td>3.6</td>
</tr>
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<td>cm 5</td>
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<td>1.5</td>
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<td>cm 8</td>
<td>2.4</td>
<td>-0.98</td>
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<tr>
<td>cm 9</td>
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<td>-9.19</td>
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</table>
An early portion of our core (32cm) indicates that several diatom genera flourished, *Aulacoseira, Cocconeis, Eunotia, Puncticulata* and *Tabellaria* (see appendix for diatom images and Fig 10). *Aulacoseira* is the only primarily planktonic form, *Cocconeis* and *Tabellaria* are epiphytic or tycoplanktonic, *Eunotia* is a primarily benthic genus and *Puncticulata* can be planktonic but prefers littoral zones of lakes. As we move up core to 10cm our diatom genus community changes slightly. At 10cm the most

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**Figure 10.** Selected diatom genera through time, by percent abundance and grouped by primary preferred habitats.
abundant genera are *Cocconeis, Eunotia, Navicula, Planothidium* and *Tabellaria* (see appendix for diatom images see Fig 10). *Cocconeis* remains very abundant in this level of the core, implying it has vegetation to cling to. This allows the genus to maximize photosynthesis and increase its population. New genera appear more abundant at this level *Navicula* which, is ubiquitous in most waters of the U.S. as a benthic form that prefers cooler waters and mesotrophic conditions. *Planothidium* is another benthic form; the growth in abundance of this species could mean the vegetation cover is removed allowing light penetration to increase. Finally at 3cm in the core, this is above the level where CuSO₄ has been continually added to the lake waters, we see a dramatic change in the diatom community. *Cocconeis* goes into severe decline and the already reduced *Puncticulata* also is almost completely gone. Three new genera appear as significantly abundant *Fragillaria, Staurosira* and particularly *Stephanodiscus* which, appears to have replaced *Puncticulata* as the major centric genus (see appendix for diatom images and Fig 10). All of these new genera are planktonic forms. From our H’ and Evenness calculations genus diversity and evenness remain equivalent through the core indicating genus substitution over increased diversity and relatively similar abundance ratios for substituted genera.

An interpretation of the diatom data shows the effects of CuSO₄ on certain genera of diatoms within the community. Before the addition of CuSO₄ the lake had more littoral and macrophyte vegetation growing. This abundant growth and nutrient rich waters allowed diatoms and algae to flourish particularly genus and species that are epiphytic or prefer shaded benthic environments. As the lake became more eutrophic near the middle of the core plenty of vegetative growth continued out into deeper areas of the lake this is
exemplified by the presence and abundance of genera such as *Cocconeis, Planothidium* and *Tabellaria*. In 2005 the input of CuSO$_4$ into the lake effectively killed off submerged macrophytes pushing back the growth to just near the littoral zone. Species like *Cocconeis* cannot effectively survive in deeper open water without macrophytes to cling to. Similarly *Puncticulata* also reduced in population as *Stephanodiscus* competes with other centric diatoms in deeper planktonic areas; other factors could include an increase in nutrients to the system. *Stephanodiscus* is very good at competing with other centric forms for nutrients. The timeframe for the addition of CuSO$_4$ at 2005 is confirmed with limited uncertainty the changes in diatom assemblages and can be used to correlate the two events.

From a metals perspective, this increase in Cu implies a completely anthropogenic driven flux far above natural baseline with further additions from other non-crustal sources such as home development or lawn fertilizer (ATSDR, 2004). Cu had a low enrichment factor in the lower half of the core (~1950’s thru the 1960’s) seeing an increase in enrichment starting near 20cm (~1980’s and 1990’s). This first increase in enrichment can be linked to construction and run-off of fertilizers from various building projects occurring in and around the park as well as population growth occurring in the area. At 10cm (~2000’s) we once again see a category increase in enrichment factor (up to moderately severe enrichment) of Cu showing a dramatic increase which, can be synchronously linked to the application of algaecides (see Fig 9).

Manganese is a very common element in the natural environment particularly in clays and weathering igneous sediments. In clays Mn$^{2+}$ is easily exchanged for other similar sized ions within the Aluminum Silicate matrix or along the negatively charged
edges of the tetrahedral lattice. Mn is also easily mobilized under oxidizing conditions and during organic decomposition (Shipley et al., 2011). Mn is tied to a variety of human activities including fossil fuel burning, metal fabrication and mining. Mn has mobility potential in reduction environments. To see if Mn migration up core has occurred and potentially contaminated the upper sediments I performed a Mn/Fe ratio analysis. This method has been commonly used to establish redox conditions in lake sediments (Melles et al., 2012). Lower ratios indicate high reduction potential as lower O₂ amounts are available in the water column and near anoxic conditions in the sediments (Naehler et al., 2013). Finally using mass depth removes error associated to porosity and interval assignment (see Fig 11).

![Graph showing Mn/Fe ratios through the core.](image)

**Figure 11.** Details Mn/Fe ratios through the core. Indications that Mn may be mobilized from lower portions of the core and migrating up core from a reducing to oxidizing environment.

Mn increases up core are likely the result of post depositional remobilization. Beyond inner core migration we may be seeing other inputs of Mn from anthropogenic source further increasing its EF in the sediments. Since 1976 Mn has been added to
gasoline as an anti-knocking agent in the form of methylcyclopentadienyl manganese tricarbonyl (MMT). Though initially added exclusively in Canada, MMT gasoline is legally used in the United States as well (see Fig 9). In 1994 the USEPA determined there was no public health risk from the use of MMT additive in gasoline (EPA, 2013), this testing was revisited in 2010 to fill gaps in the data. The conclusions remained the same, though all of these test were performed under the Clean Air Act section 211(b) with no testing done on the transport of MMT into a water system. There is little data available on the deposition rates of Mn from MMT fuel sources into sediments of water systems. There is a correlation with this data and MMT addition to fuels that could imply aerosol MMT could be carried to precipitation clouds and deposited during a rain event into the environment. Previous work has indicated some transport of MMT aerosol in an urban environment (Zayed et al., 1999) but, does not indicate the levels potentially carried and re-deposited elsewhere. Mn is also regularly associated with sewage and waste water disposal (Howe et al., 2004) and could be another source of input into the Punderson sediments. Punderson Lake has its own waste water treatment facility on site and in 2011 was re-issued a permit by the Ohio EPA to discharge waste water effluent into the lake waters (2011). This could reasonably be an additional source of Mn contamination and increased concentration seen in the enrichment factor profile plus some reduced Mn from down core that remobilized and migrated up core through the pore water (see Fig 11).

Other metals tested (As, Cu and Pb) in the core show no signs of change between layers when compared to one another. Fig 9 shows Chromium as a base line factor exhibiting little if no enrichment in the core, it also shows a near continually straight line implying that no changes in concentration are visible in the core. Other metals such as Vandium, Iron and Zinc show similar trends with no evidence of migration in the core of
trace elements and a lack of enrichment may indicate that there has been virtually no contamination do to anthropogenic inputs particularly run-off events.

The EPA introduced the Clean Air Act in 1972, which began putting more constrictive limits on air pollution and particulate matter. Remediation efforts such as the removal of Pb from gasoline, paints and toys has certainly reduced Pb overall in the environment, lead in paints was removed in 1978 and lead in gasoline completely removed by 1992. Toys and other plastic products can still contain trace lead; particularly if the toy or plastic is manufactured outside the U.S. Reduction of fossil fuel burning such as coal fire plants in major cities such as Cleveland and Akron has also reduced the impact of Pb and As on the environment and prevented continual accumulation in soils and sediments. Other ecological danger exists with metal accumulation in the sediment particularly at the sediment-surface interface (Lefort et al., 2012). As bottom waters may become hypoxic during seasonal turn over events certain elements become significantly more mobile under these conditions, particularly As and Mn. It has been shown that As is released from sediments into water during redox conditions, this allows for higher than normal concentrations to be present in the bottom waters during these hypoxic periods (Li et al., 2014). Fortunately for Punderson levels of As have been steadily decreasing over the last decade as seen in Fig 10. Arsenic therefore can be assumed to play a lesser role as a pollutant or a danger to the lake ecology. Manganese concentrations have become higher in the top of the core in recent times. Manganese is very sensitive to redox reaction and these conditions allow the element to re-mobilize and move up core. Concentrations at the water-sediment surface interface will have significantly greater concentrations of Mn in the bottom waters during hypoxic events (Lefort et al., 2012). Other common metals with less studied implications such as Copper and Manganese have not been primary
targets of remediation efforts so little is known about the direct or indirect effects they can have on an ecosystem. There is no doubt however, that excessive levels of any metal can be toxic to flora and fauna including humans. In the case of Punderson Lake increases in contamination levels of Cu are having an immediate effect on populations of diatoms, plants and algae in the lake. Several ecological impacts potentially exist from excessive Cu. Since diatoms are T1 trophic producers the potential for food web cascade increases as changes to assemblages occur. One immediate effect could be the inability of planktivores to eat the new diatoms genera that replaced the declining genus. Genera such as *Stephanodiscus* are more difficult to consume as they have silica spikes and *Puncticulata* does not. Genera of planktonic diatoms are also more likely to form colonies or chains making them difficult to swallow over most epiphytic, littoral or benthic genera that are less colonial or are solitary cells. Removal of submerged macrophytes can also destabilize the sediment; reduce availability of spawning places and food resources for insect larva. From a human perspective the absorption of excess Cu is of less concern as it is often bound in the sediments or with dead organic matter. However, bio-accumulation in top predators that may be consumed by humans such as piscivorous fish can eventual exceeds a toxic level.
Chapter VI

Conclusions

Due to the location of the lake away from major industrial production, point source pollution and major urban centers we can assume a majority of trace metal pollution is the result of atmospheric deposition in the form of precipitation and run-off during rain events. This is particularly true of elements such as Pb and As who have few other vectors of contamination related to Punderson Lake. With the metal working and chemical and industries of Cleveland and Akron in decline along with population; reduction in the use of coal fire plants, heightened levels of Pb and As are no longer accumulating at dangerous levels in the sediments of Punderson Lake. This is actually occurring based on the levels of Pb and As concentration in the Lake, as they have reduced significantly over the years to levels lower than 1950’s levels.

The two other elements tested in this thesis Cu and Mn have different vectors of input from Pb or As. Although there is a likelihood that Mn deposition increases at the top of the core may be one part remobilization within the core but, another part atmospheric deposition from MMT gasoline additives substituted for Pb during the 1990’s. The latter needs further investigation and is beyond the scope of this thesis. Unlike most of the other trace metals that likely arrived in Punderson via atmospheric transport Cu and Mn have associated direct inputs on site although also from different sources. While it is possible that some trace amounts of Cu and Mn are brought in from atmospheric deposition rain-fall events and groundwater discharge the surges in enrichment near the top of the core indicate different intensified sources. In the case of
Cu the use of herbicides and algaecides on the lake for beautification and algal bloom reductions, the input of Cu; the primary component of the herbal/algal poisons is the likely source of enrichment in lake sediments. This is confirmed with the changes in diatom assemblages. As the habitat where some genera can thrive is destroyed from the addition of CuSO$_4$, the populations of specific genera of diatoms are forced to change to meet the new habitat requirements.

Manganese is likely to be increasing through waste water and sewage effluent discharged into the lake from the properties on site waste treatment facility, as well as from re-mobilization from down core reduction environments in the sediments. Further analysis is needed to confirm the source of Mn contamination. Additional investigation deeper into the lakes history getting back into pre-industrial times could reveal a considerable amount of data relating to the ecological changes occurring in the lake system and the regional climate variations.

We can conclude that using sediment cores can be useful in elucidating a lakes recent history. This type of information can be used to develop best management practices.

- Cheaper than building a monitoring station.
- Accurately records events of pollution through time.
- Provides a big picture that accounts for the past, present and potentially the future.
- We also know that we can gauge the severity of element accumulation through the use of Enrichment factors rather than using ppm as a common measurement.

This research provided key information concerning CuSO$_4$ application to the lake.
While it is important to maintain the lake free of excessive algae and vegetation that might prevent boat travel or recreation, it is important to find a level of CuSO₄ addition that minimizes impact to the biotic communities and still reduces algal blooms.

Lake management should consider the dangers of excessive metals in lake sediments such as Punderson. Investigation of the impacts of fauna trophic cascade on the lake ecosystem is a challenge for future research. Notably piscivorous fish such as bass and habitat loss combined with diatom assemblage changes due to Cu poisoning are important items for understanding the health of the lake and any lake similar to it. Has the CuSO₄ application potentially started a trophic cascade? Can that be undone? Investigation of organic compounds to the system such as Nitrogen and Phosphorus would also be very useful for continual management of the lake. Is local application of fertilizer helping to enhance algal blooms? Would a reduction in fertilizer use reduce those blooms and hence allow for a reduction in CuSO₄ application? Sedimentation rates indicate fast burial in Punderson but, what of water residence time and downstream pollution or the impact Punderson could have on the greater watershed. Or is Punderson an excellent reservoir, acting as a holding bin for contaminates preventing downstream accumulation? There is considerable more work to be done in Punderson Lake as well as utilizing these tools and methods in other small lakes.
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Appendix

Appendix Figure 1. Punderson Lake Map with sample locations. Ohio Department of Natural Resources, 2012.
Appendix Figure 2. Punderson Lake Map with sample locations, bathometric values, small location map showing nearby major cities and county lines. Small corner map shows greater Cuyahoga river watershed and Punderson Lakes location there in.
Appendix Figure 3. Select images of diatoms from sediment core #4 of Punderson Lake Ohio. Top 3 Diatom genera are from the bottom of the core, bottom 2 are from the top of the core and the far right diatoms are common throughout the core.