

## HEAVY METAL CONCENTRATIONS AND ENVIRONMENTAL QUALITY IN THREE WISCONSIN LAKES

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### INTRODUCTION

Humans have impacted most of the Earth's surface, and lake sediments are a particularly useful means of examining that impact because they preserve biologic, geologic, and chemical data in a continuous record progressing back in time (Dietl et al., 2015). Aquatic ecosystems are more susceptible to the effects of pollution than terrestrial ecosystems, because they have less relative biomass spread over a higher order of trophic levels. Among aquatic ecosystems, lakes are especially sensitive because they serve as receptacles for effluents. (Forstner and Wittman, 1983). This study examines heavy metal pollution in three Wisconsin lakes spanning a range of environmental and human influence: Sparkling Lake is the least impacted and is found in sparsely populated northern Wisconsin; Shadow Lake, located in a small urban environment in central Wisconsin, is moderately impacted and has been chemically remediated; and Lake Monona is the most impacted in southern Wisconsin in a large urban environment.

There are two sources of heavy metals in lacustrine environments: natural processes and human processes, and there are two sources of lake pollution: terrestrial and atmospheric (Valette-Silver, 1993). Terrestrial pollution found in lakes, and consequently present in sediment archives, includes mining effluents, industrial waste, domestic and agricultural fertilizer runoff, and garbage leaching, among others (Forstner and Wittmann, 1983). These fluxes are accelerated by land clearing, because with less trees and vegetation, soil erosion and sedimentation rates are higher, and metals are brought to lakes more quickly (Kauppila, 1997). Atmospheric pollution occurs when a metal

enters the atmosphere, spreads, and is later deposited into a lake. Due to their environmental persistence, high toxicity, and the ease with which they can enter a lacustrine food chain, heavy metals have been studied extensively in sediment cores in lakes around the world (Kishe and Machiwa, 2003; Ozmen et al., 2004; Perin et al., 1997).

### LAKE SETTINGS

Sparkling Lake is the least impacted of the three lakes in this study and is considered relatively pristine. The lake is found in Vilas County, WI, and is one of thousands of kettle lakes in the area formed at the end of the last glacial maximum, 12-14 ka, by the retreating Laurentide Ice Sheet (Magnuson, 1984). Beneath roughly 40 m of sandy glacial till and outwash lies granitic basement rock (Attig, 1985). Sparkling Lake is oligotrophic, dimictic, with noncalcareous bedrock, and fed by groundwater discharge and direct precipitation and has no surface water inlets or outlets (Hoffman, 2013).

Shadow Lake is a moderately impacted, chemically remediated lake located in central Wisconsin in the small town of Waupaca (McNelly, 2012). Similar to Sparkling Lake, Shadow Lake is a kettle lake formed at the end of the last glacial maximum. The lake sits on about 50m of glacial till left by the receding Green Bay Lobe of the Laurentide Ice Sheet, beneath which is granite bedrock (Possin, 1973; Robertson, 2005). It is a drainage lake with an inlet from nearby Mirror Lake to the North and a dredged outlet to the Crystal River to the South (McNelly, 2012). Shadow Lake has been studied and monitored since the mid-1970s in the interest of improving the health of the lake and

determining the effect of the aluminum sulfate (alum) remediation applied in 1978 to combat eutrophication.

Lake Monona is located in Madison, WI, and is the most impacted of the three lakes in this study (Lathrop, 2007). Lake Monona was created by the morainic damming of the preglacial Yahara River at the end of the last glacial maximum. It is primarily a drainage lake, though fed both by groundwater and three surface water inlets, and it has one outlet to Lake Waubesa (Bortleson, 1975). Lake Monona is a eutrophic lake with a sand and gravel lake bed overlying Cambrian sandstone bedrock with some dolomite and shale (Robertson, 2005).

## PURPOSE

The objective of this study is to characterize the past and present biogeochemical state of Sparkling Lake, Shadow Lake, and Lake Monona and the influence of anthropogenic activity on these lakes. This goal will be accomplished by analyzing the heavy metal concentrations of As, Ca, Cu, Pb, Si, Ti, and Zn acquired from X-ray Fluorescence (XRF) analysis of sediment cores taken from each lake. This data will be correlated to direct observations of organic and carbonate material within the cores gathered through Loss on Ignition (LOI). These correlations will characterize what the effects of pollution and remediation have had on the lakes' ecosystems.

## METHODS

In total, thirteen lake sediment cores were taken from a small pontoon boat, only the deepest core from each lake was analyzed with XRF and is discussed in this study, since these cores are the most representative of each lake. Cores were collected using the piston corer method and a Griffith coring device in a polycarbonate tube (Wright et al., 1984). Zorbital Plus Superabsorbent Polymer, a sodium polyacrylate powder was used to gelatinize the water at the top of the core without disturbing the underlying sediment in order to best preserve the sediment-water interface of each core (Tomkins et al., 2007).

At the National Lacustrine Core Facility (LacCore) at the University of Minnesota, Twin Cities, each core was split and digitally photographed then

described using smear slides (Rothwell, 1989). For LOI, each core was sampled at 1 cm intervals in 1 cm<sup>3</sup> quantities and placed into a small, pre-weighed crucible and oven-burned three times, at 100°C, 550°C, and 1000°C to remove water, organics, and carbonate content, respectively. The crucibles were reweighed after each burn (Heiri et al., 2001), and the percentages of each component was determined with LacCore's Excel macro.

The metal concentrations of each core were acquired with XRF analysis at the Large Lakes Observatory (LLO) at the University of Minnesota, Duluth using an ITRAX X-ray Fluorescence Core Scanner (Cox Analytical Instruments) (Brown, 2011). Data was collected at a resolution of 0.5 cm and represented in output data as raw counts. The raw count at each depth was converted to concentration using known standards at LLO. Standards were unavailable for As and Pb, so they are shown in the results as a ratio of raw counts to a relatively stable element, Tungsten (W) to help reduce some of the heterogeneity inherent to sampling.

## RESULTS

There were changes in the heavy metal concentrations at all depths of the three cores, but the most variation occurred in the upper 50 cm. Sparkling Lake showed relatively stable heavy metal concentrations, though some variance was seen above 10 cm depth (Fig. 1). Cu, As, and Pb all had relatively constant levels through the core, while Ca, Si, and Zn all displayed slight increases in concentration beginning at 10 cm depth and Ti decreased in the upper 10 cm of the core.

Analysis of the Shadow Lake core (Fig. 2) exposed more fluctuation than Sparkling Lake. Cu, As, and Pb showed little change throughout the core, while Si, Ti, and Zn were stable until about 20-30 cm, above which moderate increases in concentration occurred. Ca experienced the greatest changes through the core as a whole, varying through the entire depth between 0 and 8.5 weight percent. Finally, Ca, Si, Ti, Zn, and Pb all show an abrupt spike in concentration at approximately 20 cm.

Lake Monona's core showed the greatest variability in metal concentrations across the widest range of metals (Fig. 3). Si, Ti, and Zn followed the same

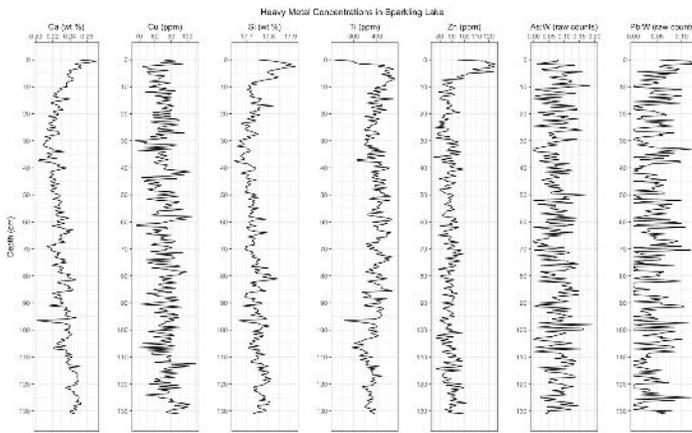


Figure 1. Heavy metal concentrations in the Sparkling Lake core (SAEQ-SPK16-1A-1P-1) are relatively stable, with fluctuations only in the upper 10 cm of sediment.

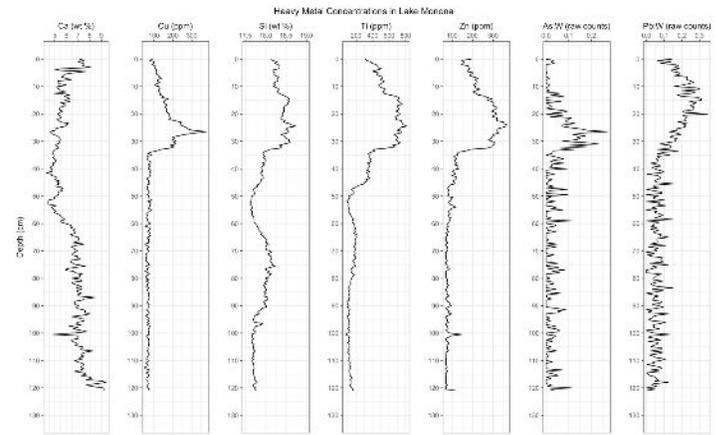


Figure 3. Heavy metal concentrations in the Lake Monona core (SAEQ-MONA16-5A-1P-1) show the greatest increases in the upper 50 cm of sediment.

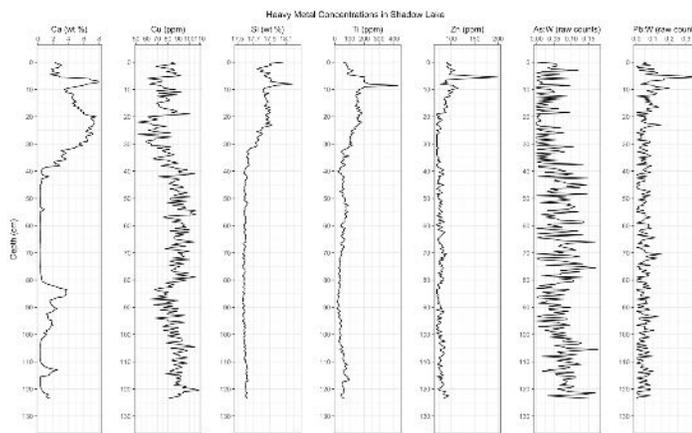


Figure 2. Heavy metal concentrations in the Shadow Lake core (SAEQ-SHOW16-1A-1P-1) increase in the upper 40 cm of sediment. The alum treatment layer is at 9 cm depth.

general trend: relatively stable concentrations until 50 cm depth, then a slow increase until 15 cm, and then a decrease in concentration to the top of the sediment. Pb displayed a constant increase in raw counts until 15 cm and then a constant decrease to the top of the core. Even after the decreasing trends in the top 15 cm of the core, the concentrations of all four of these metals (Si, Ti, Zn, and Pb) remained higher than in the bottom 50 cm of sediment. The plot of As showed an increase from near 0 beginning at 35 cm, a peak at 27 cm, and a decline and return to near 0 at 19 cm. Cu had a similar concentration trend, which rested at about 50 ppm until 35 cm, an increase and plateau of 200 ppm at 31 cm, and a peak at nearly 400 ppm at 27 cm, followed by a decrease in concentration to about 70 ppm at the top of the sediment.

## DISCUSSION

Of the three lakes, Sparkling Lake has the lowest overall metal concentrations and shows the least variability in concentrations with depth. This was expected given the lake's remote location in northern Wisconsin, low human population, and minimal land development. Relatively stable, pre-human impact levels for each metal extend from 131 cm to about 10 cm depth. The fact that certain metals (Ca, Si, Ti, and Zn) only begin to increase here suggests two things: development around the lake began more recently than near Shadow Lake or Lake Monona, and the impact has been light enough to only slightly increase sedimentation rates. The stable background concentrations and raw count ratios of Cu, As, and Pb can be attributed to the remoteness of the lake and absence of chemical treatments by humans in its history. Sparkling Lake also had the least variance in organic and carbonate content of the three lakes, reflecting a relatively constant biologic output.

The work of Iskandar and Keeney (1974) provides a useful comparison to Sparkling Lake. Their study examined the heavy metal concentrations of nearby Mary Lake, located in the same county with a similar cultural and geologic setting. Its core, as in the case of Sparkling Lake, has relatively stable background levels of most metals, but Iskandar and Keeney did find Pb concentrations to be consistently less than 0.1 ppm until the upper 5 cm of sediment, when they rose to about 3 ppm. They attribute this increase

in Pb to atmospheric loading and fallout, and it therefore seems likely that Pb concentrations in the upper few centimeters of sediment in Sparkling Lake could also be elevated. Iskandar and Keeney used Spectrophotometry rather than XRF to determine metal concentrations, and their methodology could have been more sensitive than XRF to low Pb concentrations.

Shadow Lake has higher heavy metal concentrations than Sparkling Lake but lower than Lake Monona, as well as moderate changes in the physical core, which was also anticipated because of the lake's small urban environment. The most striking part of Shadow Lake's XRF data is the abrupt spike in Ca, Si, Ti, Zn, and Pb at about 10 cm depth (Fig. 2) as a result of the alum treatment, and they correlate with the thin layer of alum seen in the physical core at the same depth. None of the elements in the alum compound are heavy enough to be detected by XRF, which may explain the apparent increases in metal concentrations. The general increases of Si, Ti, and Zn from 35 cm up can be attributed to the land development by settlers starting around 1850. Ca displays the greatest change in concentration through the core, which strongly correlates with the LOI analysis and physical changes in the core. For example, the high Ca concentrations between 8 cm and 45 cm is also where LOI shows a low organic component (generally 20 weight percent or less). In contrast, from 45 cm to 82 cm depth, where Ca concentrations are less than 1 weight percent, LOI shows sediment rich in organics (60 to 80 weight percent).

The heavy metal concentrations of Lake Monona are the highest and most varied of the three lakes. As with Shadow Lake, concentrations of Si, Ti, and Zn start to increase at 50 cm due to land development and erosion as land was cleared by European settlers (Fig. 3). Since the Madison area was developed at about the same time as Waupaca (1850), the fact that Lake Monona's impacted depth is about 15 cm lower suggests a higher sedimentation rate than Shadow Lake, resulting from natural and/or human causes.

The levels of Cu, As, and Pb agree with the documented environmental history of Lake Monona. Both Cu and As sharply increase in concentration at 34 cm depth (Cu from a stable background level of 50

ppm first up to 200 ppm, then to nearly 400 ppm at 27 cm). These increases are undoubtedly a result of the routine chemical treatments for weeds by the Madison Public Health Department from the mid-1920s to the mid-1950s in the case of Cu and the mid-1960s in the case of As (Lathrop, 2007). While the amount of As in the sediment seems to return to background levels by 20 cm, the Cu concentrations decrease more slowly and remain slightly above background levels at the top of the sediment. Perhaps the Cu deposited the sediment has migrated upward even after the treatments ended, while As has stayed where it was directly deposited. Pb shows a much more prominent increase than in Sparkling and Shadow Lakes, increasing from about 40 cm to 20 cm then decreasing until the top of the core. Following the reduction in leaded gasoline in the 1970s, the amount of Pb in the atmosphere has declined as it slowly fluxes to geologic sinks such as lake sediments through fallout.

As the best studied of the three lakes, previous work by other researchers offers important comparisons to Lake Monona as well as context for the data from Sparkling and Shadow Lakes. The Cu concentrations published by Lathrop (2007) show a similar trend to the one outlined above with XRF, but with notably different concentrations. Lathrop found Cu to have a peak of about 800 ppm, whereas this study found a peak of slightly less than 400 ppm. In further contrast, the study by Iskandar and Keeney (1974) also examined Lake Monona, and while it too showed a similar trend of Cu concentration, it found a maximum concentration of 510 ppm. These studies each used different methodologies, and while these discrepancies do reduce the confidence in the accuracy of the heavy metal concentrations, it does increase confidence in the precision of the concentrations as well as in the general trends of the metals.

## CONCLUSION

The goal of this project was to establish the heavy metal concentrations of these three lakes, determine if any relationship exists between changes in the metal concentrations and the biology of the lakes, and assess the human impact on the lake ecosystems. The XRF data demonstrates that many heavy metals did change in concentration through the cores as the result of both natural and anthropogenic activity. Some increases

in heavy metal concentrations, including Si, Ti, and Zn, can be broadly attributed to land clearing and development, while others such as Cu, As, and Pb can be tied to specific moments in the environmental history of the lakes.

Human activity has left its permanent mark even on some of the most seemingly insignificant material: buried mud. Compared to relatively “pristine” Sparkling Lake, which itself showed small increases in heavy metal concentrations, the human impact on the other two lakes is unmistakable. Shadow Lake and especially Lake Monona have experienced dramatic changes to their heavy metal concentrations, and even after intense anthropogenic forces have ceased, elements such as Cu could still be mobile and influencing the ecosystem.

#### ACKNOWLEDGEMENTS

Thank you to The Keck Geology Consortium, The National Science Foundation, and ExxonMobil Corporation for a year of engaging science, my advisor Pat Spencer, Jill Leonard-Pingel and Andy Michelson for all their work leading our research, Amy Myrbo and Kristina Brady at LacCore for their expertise and guidance, Aaron Lingwall at LLO for his patience and skill running the XRF, each of the other five students in our team, as well as Bryn Kimball and Nick Bader for their help with data analysis.

#### REFERENCES

- Attig, J.W., 1985, Pleistocene Geology of Vilas County, Wisconsin: Wisconsin Geological and Natural History Survey, p. 4.
- Blais, J.M., and Kalff, J., 1993, Atmospheric loading of Zn, Cu, Ni, Cr, and Pb, to lake sediments: the role of catchment lake morphometry, and physico-chemical properties of the elements: *Biogeochemistry*, vol. 23, no. 1, p. 1-22.
- Bortleson, G.C., 1975, Recent sedimentary history of Lake Monona, Wisconsin: *Water, Air, and Soil Pollution*, no. 4, p. 89-98.
- Brown, E.T., 2011, Lake Malawi’s response to “megadrought” terminations: Sedimentary records of flooding, weathering and erosion: *Palaeogeography, Palaeoclimatology, Palaeoecology*, no. 303, p. 120-125.
- Dietl, G. P., Kidwell, S. M., Brenner, M., Burney, D. A., Flessa, K. W., Jackson, S. T., and Koch, P. L., 2015, Conservation Paleobiology: Leveraging knowledge of the past to inform conservation and restoration: *Annual Review of Earth and Planetary Sciences*, no. 43, p. 79-103. doi:10.1146/annurev-earth-040610-133349.
- Forstner, U., and Wittman, G.T.W., 1983, *Metal pollution in the aquatic environment*: Springer.
- Heiri, O., Lotter, A. F., and Lemcke, G., 2001, Loss on ignition as a method for estimating organic and carbonate content in sediments: Reproducibility and comparability of results: *Journal of Paleolimnology*, no. 25, p. 101-110.
- Hoffman, A.R., Armstrong, D.E., and Lathrop, R.C., 2013, Influence of phosphorus scavenging by iron in contrasting dimictic lakes: *Canadian Journal of Fisheries and Aquatic Sciences*, no. 70, p. 941-952.
- Iskandar, I. K., and Keeney, D. R., 1974, Concentration of Heavy Metals in Sediment Cores from Selected Wisconsin Lakes: *Environmental Science and Technology*, no. 8, p. 165-170.
- Kaupilla, T., and Salonen, V.-P., 1997, The effect of Holocene treeline fluctuations on the sediment chemistry of Lake Kilpisjärvi, Finland: *Journal of Paleolimnology*, no. 18, p. 145-163.
- Kishe, M. A., and Machiwa, J. F., 2003, Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania: *Environment International*, no. 28, p. 619-625.
- Koinig, K.A., Shoty, W., Lotter, A.F., Ohlendorf, C., and Sturm, M., 2003, 9000 years of geochemical evolution of lithogenic major and trace elements in the sediment of an alpine lake - the role of climate, vegetation, and land-use history: *Journal of Paleolimnology*, no. 30, p. 307-320.
- Lathrop, R. C., 2007, Perspectives on the eutrophication of the Yahara lakes: *Lake and Reservoir Management*, no. 23, p. 345-365.
- Magnuson, J.J., Bowser, C.W., and Kratz, T.K., 1984, Long-term ecological research (LTER) on north temperate lakes of the United States: *Verhandlungen des Internationalen Verein Limnologie*, no. 22, p. 533-535.
- McNelly, J., and Turyk, N., 2012, *Mirror and Shadow Lakes Management Plan*: Friends of Mirror

- and Shadow Lakes Management Planning Committee, [http://www.cityofwaupaca.org/parksnrec/wp-content/uploads/sites/3/2014/05/Mirror\\_Shadow\\_Lk\\_Mgt\\_2013.pdf](http://www.cityofwaupaca.org/parksnrec/wp-content/uploads/sites/3/2014/05/Mirror_Shadow_Lk_Mgt_2013.pdf).
- Ozmen, H., Kulahci, F., Cukurovali, A., and Dogru, M., 2004, Concentrations of heavy metal and radioactivity in surface water and sediment of Hazar Lake (Elazig, Turkey): *Chemosphere*, no. 55, p. 401-408.
- Perin, G., Fabris, R., Manente, S., Wagener, A.R., Hamacher, C., and Scotto, S., 1997, A five-year study on the heavy-metal pollution of Guanabara Bay sediments (Rio de Janeiro, Brazil) and evaluation of the metal bioavailability by means of geochemical speciation: *Water Resources*, vol. 31, no. 12, p. 3017-3028.
- Possin, N. B., 1973, The hydrogeology of Mirror and Shadow Lakes in Waupaca, Wisconsin [M.S. thesis]: University of Wisconsin Stevens Point.
- Robertson, J. M., 2005, Bedrock geology of Wisconsin: UW Extension, Wisconsin Geological and Natural History Survey.
- Rothwell, R.G., 1989, Minerals and mineraloids in marine sediments; an optical identification guide: Elsevier Appl. Sci, London, United Kingdom.
- Tomkins, J. D., Antoniades, D., Lamoureux, S. F., and Vincent, W. F., 2008, A simple and effective method for preserving the sediment-water interface of sediment cores during transport: *Journal of Paleolimnology*, vol. 40, no.1, p. 577-582.
- Valette-Silver, N. J., 1993, The Use of Sediment Cores to Reconstruct Historical Trends in Contamination of Estuarine and Coastal Sediments: *Estuaries*, vol. 16, no. 3, p. 577-588.
- Wright, H. E., Jr., Mann, D. H., and Glaser, P. H., 198