Antifouling Paints: heavy metals pollution in Lake Macatawa

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Abstract

The effect of pollution on freshwater resources, such as Lake Macatawa, is a concern for not only those who recreationally use the lake and the organisms whose habitat is in Lake Macatawa, but also for the composition of the lake as a whole. The pollutant this study focused on was copper. One way traces of heavy metals, like copper, can be integrated into the sediment of lakes is through the use of ablative antifouling paints on the hulls of boats. Antifouling paints contain biocides, which help reduce the amount of bio-build up by killing off any algae or invertebrates that adhere to the boat's surface. Until the 1980's, antifouling paints used a toxic chemical known as TBT (tributilin), a class of organotin compounds. However, because of its toxicity to a large range of organisms, it has been banned across the globe. Alternative biocides have now been introduced mainly consisting of copper oxide paint accompanied by organic biocide boosters. In the same way that these biocides are toxic to the fouling organisms on the hulls of boats, they can also become toxic to the surrounding aquatic life as the chemicals used in the paints begin to build up in the sediment. Many of the biocides used in antifouling paints, such as copper, tend to be persistent in nature and pose many potential environmental problems as their concentrations exceed natural levels. Data on copper accumulation in sediment was taken at five marinas along Lake Macatawa. Control sediment samples were taken at two locations outside of the marinas on Lake Macatawa in order to represent the background levels of copper. Results indicated that trace amounts of copper and lead are present within the sediment of Lake Macatawa marinas, and suggest that the copper concentrations in the sediment of "cleaning" stations may be significantly higher when compared to other sampling sites within the marina.

Introduction

Antifouling paints have been known to cause heavy metal pollution in lakes. Copper, one of the main toxins used in antifouling paints today, is an essential nutrient, but within organisms' cell tolerance limits. Toxins stay in the sediment even after vessels leave, and the harmful effects of copper can cause problems with organisms' neural processes, reproduction, metabolism, protein function and chemosensory abilities, to name a few.

A study was conducted in 2013 from Ohio State and Bowling Green State Universities titled "Copper Concentrations at Lake Erie Marinas." The expectations of this study was that boat bottom washing at marinas would increase copper concentrations in the sediment and water, and that copper concentrations would differ throughout the marina. Their goals were to conclude that copper concentrations in near-shore sediments were due to boat bottom wash wastewater, while also providing data to enable locals to make informed decisions when choosing sustainable paints. Results showed that marinas had a significantly higher copper concentration than channel controls and that samples taken from wash sites had significantly higher copper concentrations

than dock sites. This study also concluded that marinas that offered hull washing services had significantly higher copper concentrations than those that did not.

To further explore this trend, our research is focused on the presence of copper in the sediment of Lake Macatawa from antifouling paints and boat bottom wash wastewater. When a significant concentration of copper was found in the sediment of Lake Macatawa, we looked into the differences of copper concentrations in the sediment based on sample location. To further study this concept, samples of sediment were taken at marina areas and non-marina areas around the lake. After a significantly higher concentration was found within the marina areas, samples were taken at different locations within marins. The presence of any other heavy metal in the sediment sample was also researched.

Materials and Methods

To research the concentration of copper in the sediment of Lake Macatawa, five marinas and three control locations were sampled throughout the fall months of September, October and November. At each marina samples were taken from the boat-haul out/cleaning area and various dock locations away from the designated cleaning station. The marinas sampled on the north side of Lake Macatawa include Parkside Marina, Yacht Basin Marina and Anchor Marina. The control locations sampled on the north side of the lake include Black Lake Boardwalk and Howard B. Dunton Park. On the south side of Lake Macatawa, the marinas sampled include Eldean's Shipyard and the Macatawa Bay Yacht Club (MBYC). The control location sampled on the south side of Lake Macatawa was Kollen Park.

A Wildco grab sampler was used to obtain sediment samples from each of the sampling locations. After sediment was collected in the grab sampler, the sediment was moved to labeled bags and taken back to the lab to analyze. Samples were placed in a chemical hood with an air filtration system until dried. Several samples were then mounted on specialized carbon tape in order to be surveyed for heavy metals using a scanning electron microscopy coupled with electron dispersive x-ray spectroscopy. Samples were then prepped for Atomic absorption spectroscopy (AA) following the procedures of Tsunemasa et al. (2014). This acid digestion procedure uses a 3:1 ratio of concentrated Nitric to hydrochloric acid to extract any environmentally available heavy metals from the sediment. Following the acid digestion samples were vacuum filtered to remove any suspended sediment and then diluted to 100mL using RO water. Previous to running samples on the AA instrument, lead and copper standards purchased from Sigma Aldrich were diluted into 1, 2, 4, and 5 ppm solutions in order to make Beer's Law Plots. The Beer's law plots graphed the known concentrations of the lead and copper standards versus the measured absorbance values, which gave us a linear equation that was used to calculate the metal concentrations in our sediment samples using their measured absorbance values.

Results

Our initial SEM/EDS results from the Anchor marina, Howard Donton park, and the MBYC showed that there was copper and lead present in the majority of our sediment samples

(Fig.1) . From our AA results found that four out of the five marinas we sampled from had elevated copper concentrations when compared to the non-marina control sites (Fig. 2). These marinas include Yacht Basin, Eldean's, MBYC, and the Anchor marina and had copper concentrations of 211.34, 31.88, 29.51, and 11.22 mg/kg respectively. Yacht basin had the highest concentration of copper in the sediment by far. We sampled from four locations within the Yacht Basin marina, including the "Cleaning site", Right, Left A, and Left B. The copper concentrations at each of these sites were 658.10, 160.56, 46.92, and 6.5 mg/kg respectively (Fig. 3). Of the four sites within Yacht Basin, we noticed that the "Cleaning site" had the highest copper concentration on average, suggesting this may be a point of copper contamination. Using the Department of Environmental Conservation's (DEC's) freshwater sediment guidance values, we were able to evaluate the quality of sediment at each of the marinas (Table 1) We found that only Yacht Basin had a copper concentration above the DEC's consideration for contaminated sediment, and qualified as highly contaminated by copper (Table 2). Our AA results for lead showed that there were very low levels of lead in all five of the marinas as well as the non-marina control sites. Yacht Basin, Eldean's, MBYC, Anchor Marina, Parkview, and the non-marina controls had lead concentrations of 10.86, 0.00,11.09, 0.00, 7.05, and 1.88 mg/kg respectively. These were all below the DEC's consideration for freshwater sediment contamination by lead.

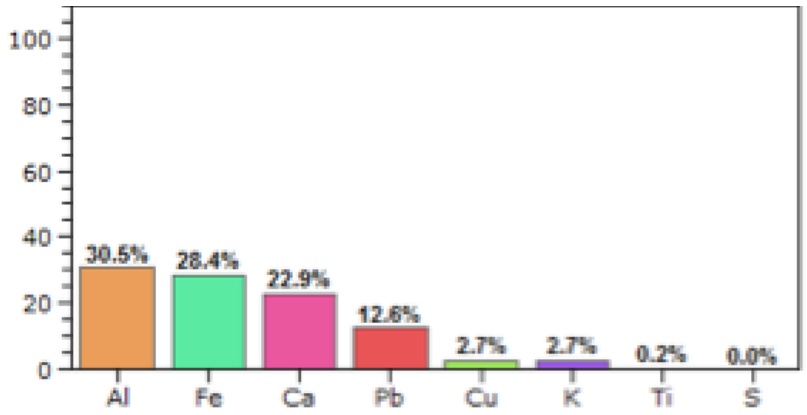

Figure 1. Bar graph showing the percent of metals present in sediment in relation to those selected for using SEM/EDS. Results show that copper and lead are present.

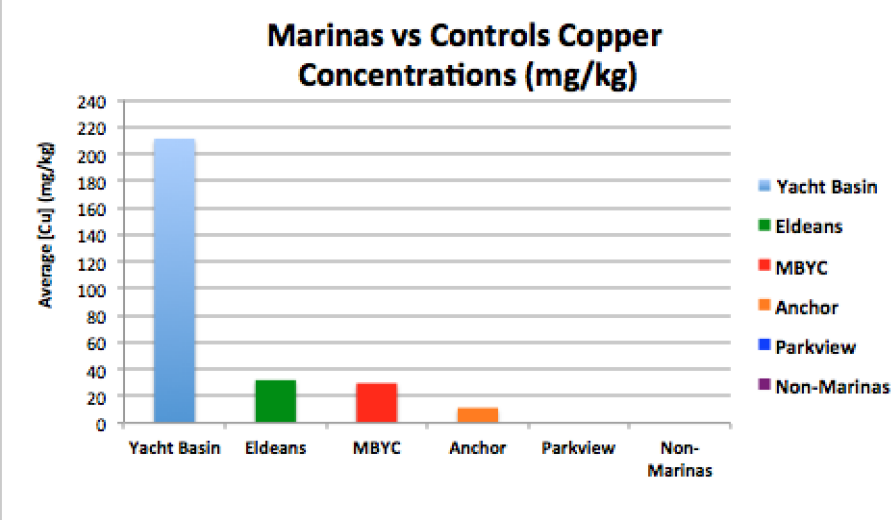

Figure 2.) Bar graph showing the average copper concentration in the sediment of each marina. The concentrations for Yacht Basin, Eldeans, MBYC, Anchor, Parkview, and Non-marinas were 211.34 , 31.88, 29.51, 11.22, 0.00, and 0.00 mg/kg respectively.

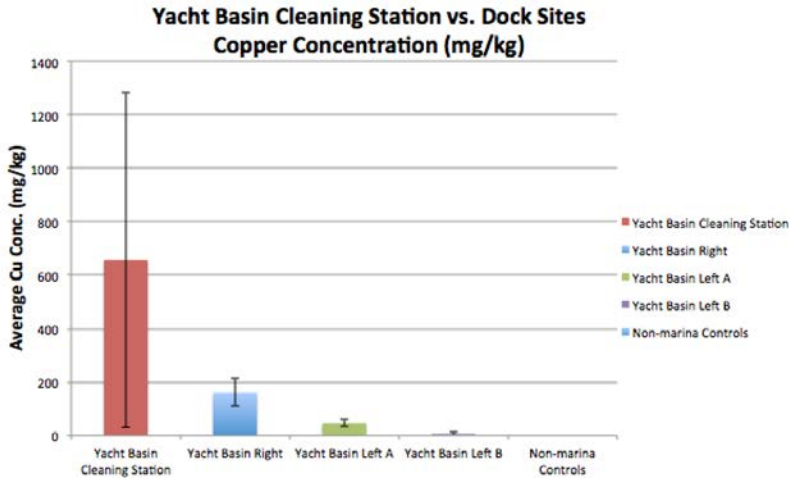

Figure 3.) Bar graph showing the average copper concentrations at four sampling locations in the Yacht Basin marina compared to non-marina controls: YB Cleaning station (658.10 mg/kg), YB Right (160.56 mg/kg), YB Left A (46.92 mg/kg), YB Left B (6.50 mg/kg), Non-marina controls (0.00 mg/kg)

Compound	Class A	Class B	Class C	Derivation
Metals, mg/kg or PPM				
Arsenic	< 10	10 – 33	> 33	1
Cadmium	< 1	1 – 5	> 5	1
Chromium	< 43	43 – 110	> 110	1
Copper	< 32	32 – 150	> 150	1
Lead	< 36	36 – 130	> 130	1

Table 1. Freshwater sediment guidance values as defined by the DEC. Class A sediments are considered to be of low risk to aquatic life. Class B sediment are slightly to moderately contaminated and additional testing is required to evaluate potential risks to aquatic life. Class C sediments are considered to be highly contaminated and likely to pose a risk to aquatic life. All values are dry weight values rounded to two significant digits.

Sample Sites	Ave. Copper (mg/kg)	Sediment Grade
Yacht Basin	211.34	C
Eldeans	31.88	A
MBYC	29.51	A
Anchor	11.22	A
Parkview	0.00	A
Non-Marinas	0.00	A
Cleaning Stations	147.40	B
Marina Docks	49.15	B

Table 2. Evaluation of Lake Macatawa marinas and Non-marina control sites sediment based on their average copper concentrations compared to the DEC's freshwater sediment values for copper contamination of sediment. Class A sediment (<36 mg/kg), Class B sediment (36-150 mg/kg), Class C sediment (>150 mg/kg). The following sampling sites were evaluated with each of their perspective sediment grades in parentheses: Yacht Basin (C) , Eldeans (A), MBYC (A), Anchor (A), Parkview (A), Non-Marinas (A), Cleaning Stations (A), and Marina Docks (A).

Discussion

Future research could include increased sampling at each marina to further determine the cause and effect of different copper concentrations found in the sediment within each marina. Since this study solely analyzed samples taken in the fall, future research could include sampling

and analyzing copper concentrations in the sediment throughout the entire year and boating season. It would be beneficial for future research to also include metadata such as the number of boats per marina, the size of boats, the availability of hull washing at each marina and the frequency of marina dredging.

Since our sampling method used a grab sampler, it was not possible to analyze concentrations correlated to specific years. In the future, research could include using a core sampler in order to analyze using radiometric dating. Using a core sampler would also be beneficial in noting the difference in heavy metal concentrations throughout the time TBT was used and when it was banned and replaced with copper.

Acknowledgments

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