

Antifouling Paints: heavy metals pollution in Lake Macatawa



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Background: Anti-fouling paints

- Fouling: growth and colonization of microorganisms on a boat's hull
- Paints used on boat hulls to slow the growth of aquatic organisms on the hull's surface
- Paints formerly used a biocide known as Tributyltin, or TBT
- TBT banned in 1980s; many paints started to use copper as a replacement chemical





Background: Paint pollution in lakes

- Copper is an essential nutrient, but within cell tolerance limits
- Toxins stay in the sediment even after the vessels leave
- Harmful effects on aquatic life and benthic organisms if cell tolerance limit is exceeded
 - Neural processes
 - Reproduction
 - Metabolism
 - Protein function
 - Chemosensory abilities - affects interactions between predator and prey
- Habitat and water quality concerns
 - Coastal ecosystems near urban areas



“Copper Concentrations at Lake Erie Marinas”

- Similar study conducted in 2013
- Ohio State University & Bowling Green State University
- Expectations
 - Boat bottom washing at marinas would increase copper concentrations in the sediment and water
 - Copper concentrations would differ throughout marina
- Goals
 - Contribution of boat bottom wash wastewater to copper concentrations in nearshore sediments
 - Provide data to enable locals to make informed decisions when choosing sustainable paints
- Results
 - Marinas had significantly higher copper concentration than channel controls
 - Samples taken from wash sites had significantly higher copper concentrations than dock sites
 - Marinas that offered hull washing services had significantly higher copper concentrations than those that did not



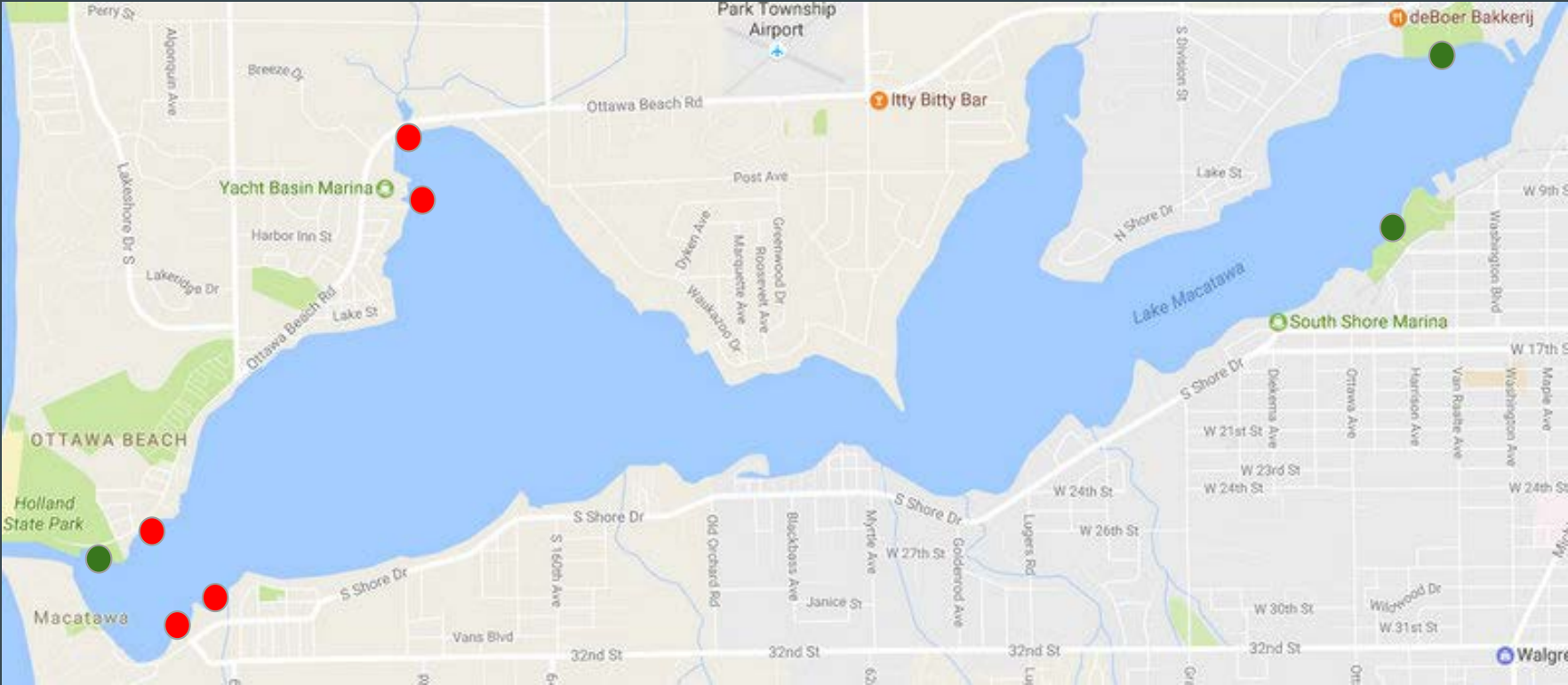
Research Questions

- Is there a significant concentration of copper in the sediment of Lake Macatawa?
- Is there a difference in concentration of copper based on where sediment samples were taken?
 - Near and far from boat-haul out areas within marinas
 - Near and far from marinas
- Are there any other heavy metals of concern found in the sediment samples?

Collecting Samples



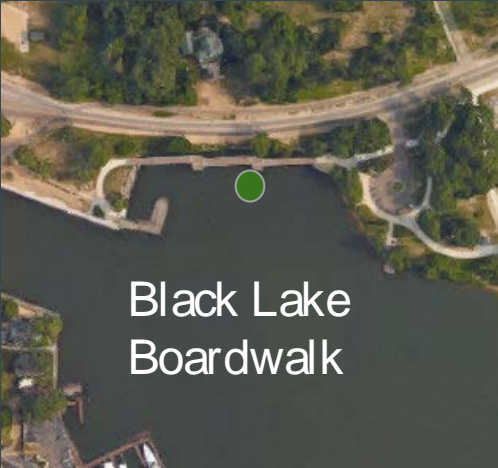
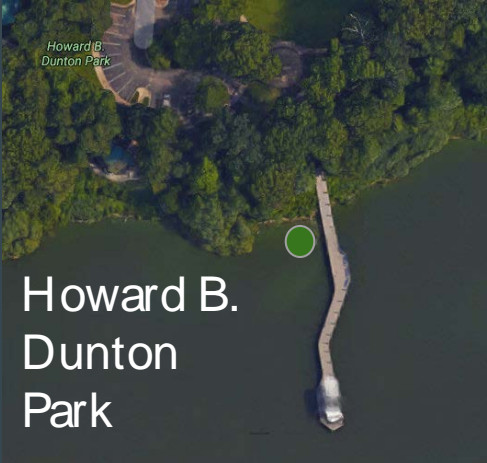
Sample Locations





Control Samples

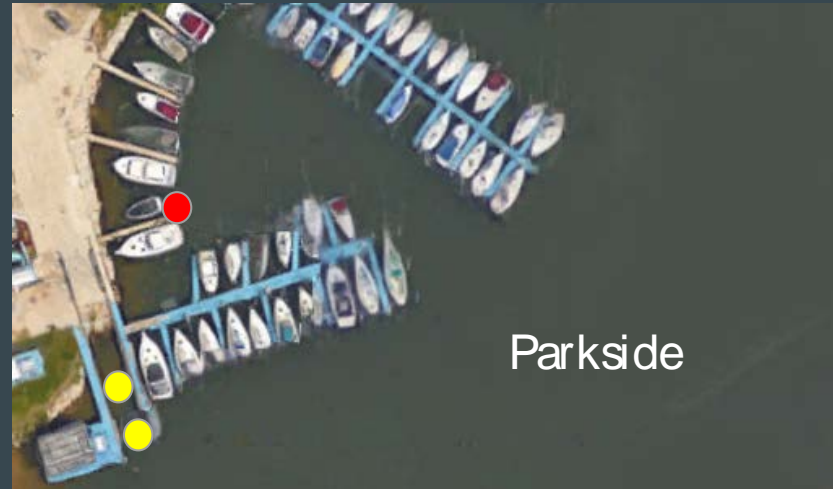
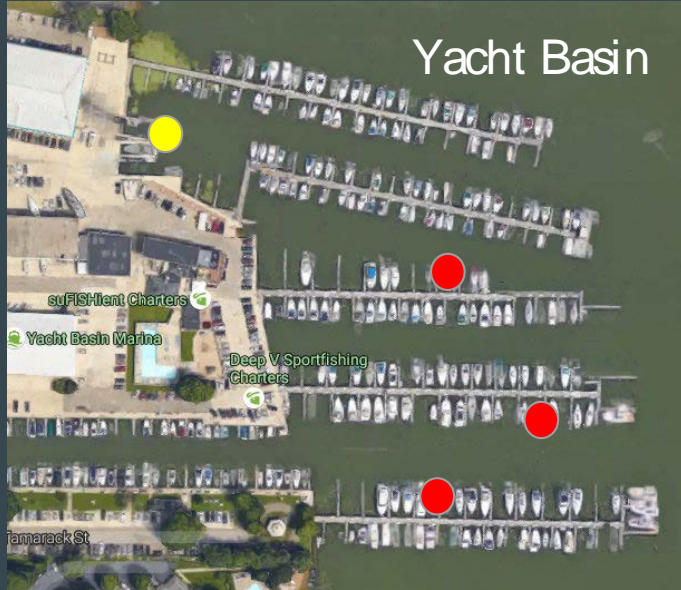
North Side



South Side



North Side: Marinas



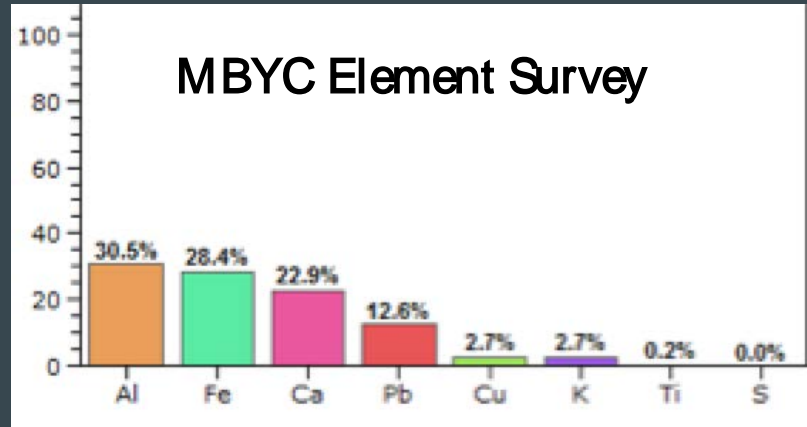


South Side: Marinas



Methods

- Scanning Electron Microscopy/ Electron Dispersive X-Ray Spectroscopy (SEM/EDS)
 - Survey of sediments for heavy metals
 - Copper and Lead present



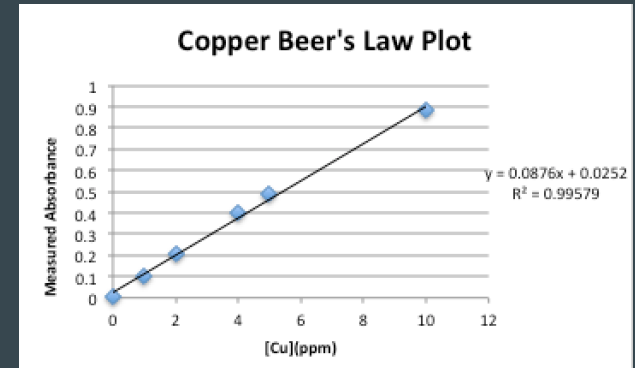
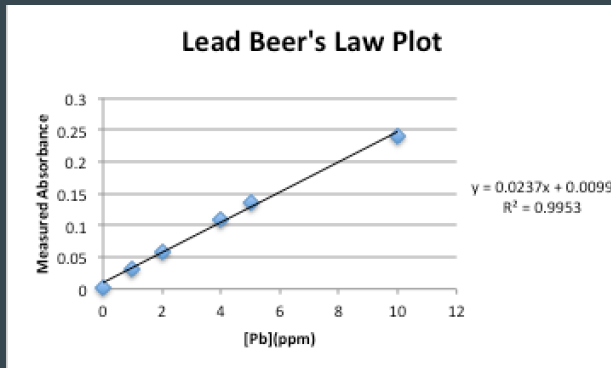
Methods

- Acid digestion of environmentally-available heavy metals
 - Following procedures from Tsunemasa et al. (2014)



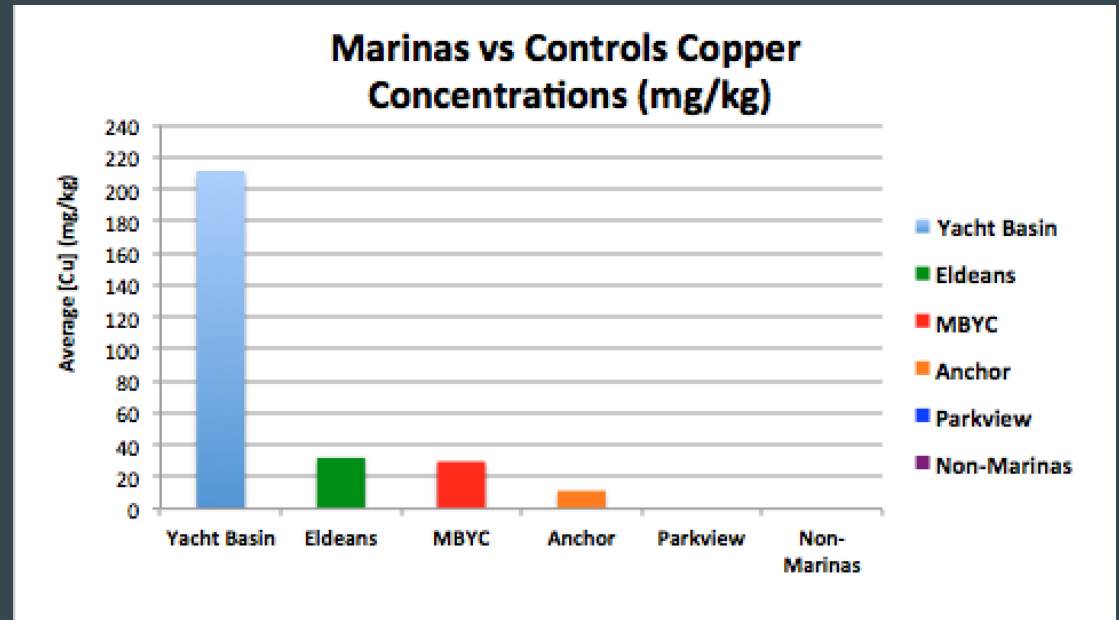
Methods

- Flame Atomic Absorption Spectroscopy (AA)
 - High sensitivity
 - Detection limits of lead= .05 mg/kg (dry weight)
 - Detection limits of copper= 5 mg/kg (dry weight)



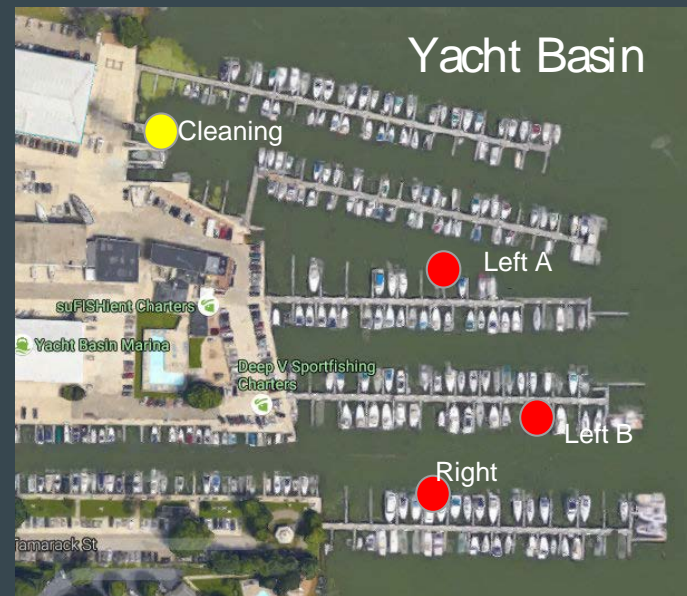
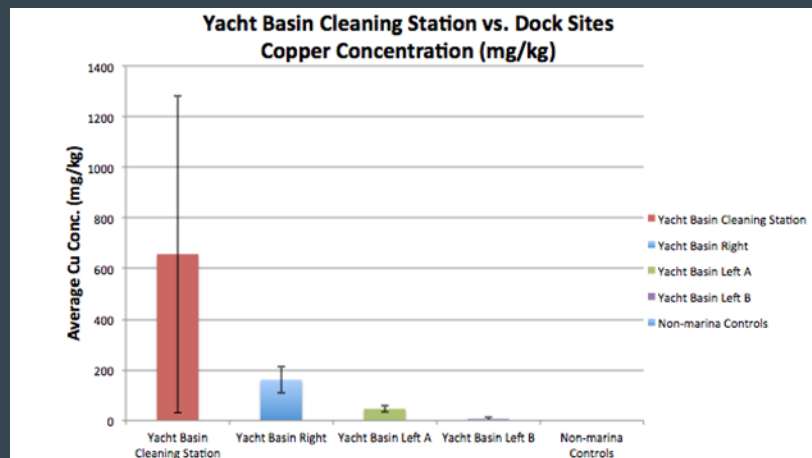
AA Results: Copper

- Elevated copper levels in 4 of 5 marina
- No copper found in non-marina sites



Yacht Basin

- Copper concentration in sediment varied throughout marina
- Highest copper concentration at marina cleaning site



AA Results: Copper Overview

DEC lim

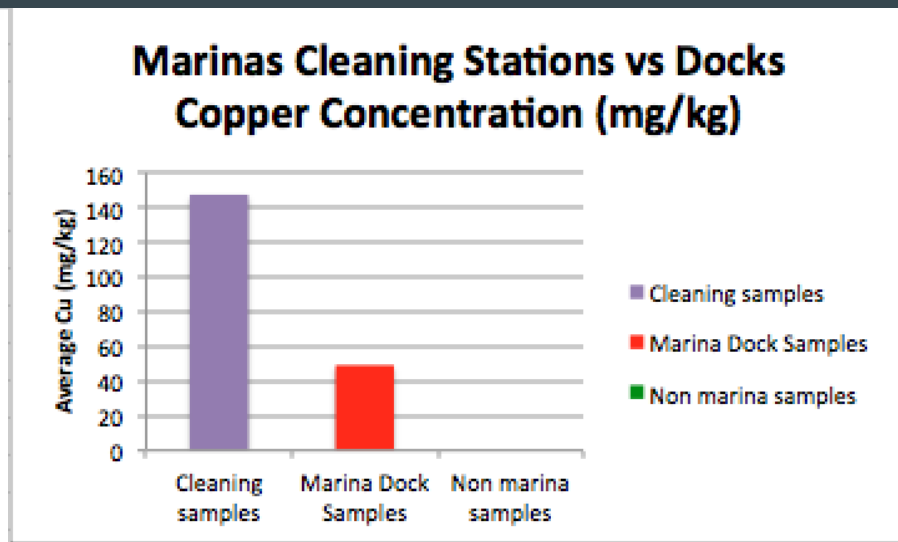
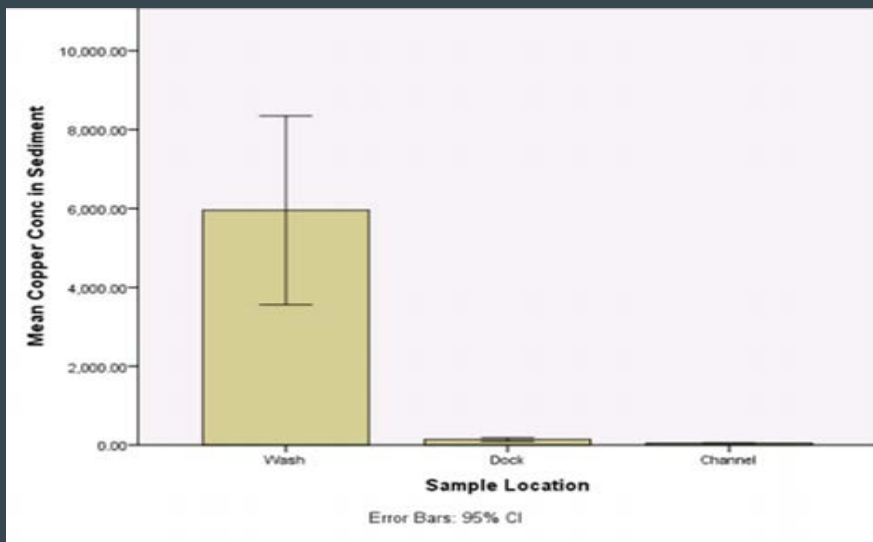
Sample Sites	Ave. Copper (mg/kg)	Soil Grade
Yacht Basin	211.34	C
Eldeans	31.88	A
MBYC	29.51	A
Anchor	11.22	A
Parkview	0.00	A
Non-Marinas	0.00	A
Cleaning Stations	147.40	B
Marina Docks	49.15	B

AA Results: Lead

All lower than DEC limit: > 36 mg/kg

Sampling Site	Ave. Lead (mg/kg)
Anchor	0.00
Eldeans	0.00
Non-Marina Locations	1.88
MBYC	11.09
Parkview	7.05
Yacht Basin	10.86
Positive Samples	24.39

Comparison of Our Results with Lake Erie Study



Lake Erie Study: Wash 3917.23 mg/kg, Dock 43.34 mg/kg, Channel 0 mg/kg

Lake Mac Study: Cleaning 147.40 mg/kg, Dock 49.15 mg/kg, Non-marina 0 mg/kg

Future Research

- More in depth sampling at each marina
- Test over length of boating season
 - Spring, Summer, Fall
- Obtain metadata
 - Number of boats per marina
 - Size of boats
 - Availability of hull washing
 - Frequency of dredging
- Historical core samples
 - Radiometric dating
 - Change in copper concentration after TBT ban

References

- Dris, Rachid, Hannes Imhof, Wilfried Sanchez, Johnny Gasperi, Fran Ois Galgani, Bruno Tassin, and Christian Laforsch. "Beyond the Ocean: Contamination of Freshwater Ecosystems with (micro-)plastic Particles." *Environ. Chem. Environmental Chemistry* 12.5 (2015): 539. *Beyond the Ocean: Contamination of Freshwater Ecosystems with (micro-) Plastic Particles*. HAL, Mar. 2015. Web.
- Harvey, Fiona. "Microplastics Killing Fish before They Reach Reproductive Age, Study Finds." *The Guardian*. Guardian News and Media, 02 June 2016. Web. 21 Sept. 2016.
- Kreefoot, Brix, and Marvin. "GLEAM." *Copper in Great Lakes Sediments*. GLEAM, n.d. Web. 21 Sept. 2016.
- Kwan, Christopher Kent, Eric Sanford, and Jeremy Long. "Copper Pollution Increases the Relative Importance of Predation Risk in an Aquatic Food Web." *PLOS ONE PLoS ONE* 10.7 (2015): n. pag. Web.
- "Multi-Species Ecotoxicity Assessment of Petroleum-Contaminated Soil." *Soil and Sediment Contamination* 12.2 (2003): 181-206. *New York State Department of Environmental Conservation Division of Fish, Wildlife and Marine Resources*. Web.
- "The Potential Effects of Antifouling Paints from Water-based Recreation." *The Potential Effects of Antifouling Paints from Water-based Recreation*. N.p., n.d. Web. 21 Sept. 2016.
- Sakkas, Vasilios A., Ioannis Konstantinou K., Dimitra Lambropoulou A., and Triantafyllos Albanis A. "Survey for the Occurrence of Antifouling Paint Booster Biocides in the Aquatic Environment of Greece." *Environmental Science and Pollution Research Environ Sci & Pollut Res* 9.5 (2002): 327-32. Web.
- Tsunemasa, Noritaka, and Hideo Yamazaki. "Result Filters." *National Center for Biotechnology Information*. U.S. National Library of Medicine, June 2014. Web. 21 Sept. 2016.

Thank You!

Dr. Brian Bodenbender

Macatawa Bay Yacht Club

Dr. Kenneth Brown

Eldean's Shipyard

Dr. Beth Anderson

Yacht Basin Marina

Dr. Graham Peaslee

Anchor Marina

Parkside Marina