

The Effectiveness of the Upper Macatawa Area Restoration

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INTRODUCTION

Lake Macatawa in Ottawa County, Michigan has long been plagued by excess nutrients causing it to become hypereutrophic. Algal blooms and turbid waters characterize the lake. Historically, the Macatawa River has burdened the lake with phosphorus-laden sediment from upstream farms with drainage tiles to the river. As one of the most eutrophic lakes in Michigan, the Michigan Department of Environmental Quality (MDEQ) developed a total maximum daily load (TMDL) for phosphorus in Lake Macatawa in 1997 (MDEQ, 2007). Since then, efforts have been made by local groups such as the Macatawa Area Coordinating Council (MACC) and the Macatawa Greenway Partnership (MGP) to reduce the phosphorus loading into the lake.

A major area of focus in reducing phosphorus loading has become the Upper Mac on account of the runoff from farms there. In 2004, drainage tiles were broken, drainage ditches were plugged, 125 acres of wetlands were restored, and retention ponds were created in the Upper Mac (MGP, 2006). Additional retention ponds were added and a meander was re-engineered for the river from 2006 to 2007 (MGP, 2006). All of the work in the Upper Mac is expected to reduce phosphorus loading into Lake Macatawa by 16,230 pounds per year (Resource Management Group, Inc., 2001). This would be a 12% reduction from the 2001 loading of 138,000 pounds per year of phosphorus and an 18% contribution to the target reduction of 91,000 pounds per year of phosphorus (Resource Management Group, Inc., 2001).

The area of focus for this project is the retention ponds created in 2003 and 2006. The hypothesis is that phosphorus should have accumulated in the sediment of the ponds since their creation, meaning that top layers of sediment should contain higher levels of phosphorus than deeper layers. To test this, sediment cores were taken from multiple ponds and river sites and comparisons were made between the sites and within the cores themselves. This hypothesis

assumes that sediment removed to create the ponds allowed for a baseline to which any new phosphorus accumulation is resultant from the ponds collecting water and sediment containing phosphorus. Water was also collected to investigate whether any correlation of phosphorus concentrations in the water and sediment exists. All samples were analyzed using Inductively-Coupled Plasma Spectrometry (ICP).

SITE DESCRIPTIONS:

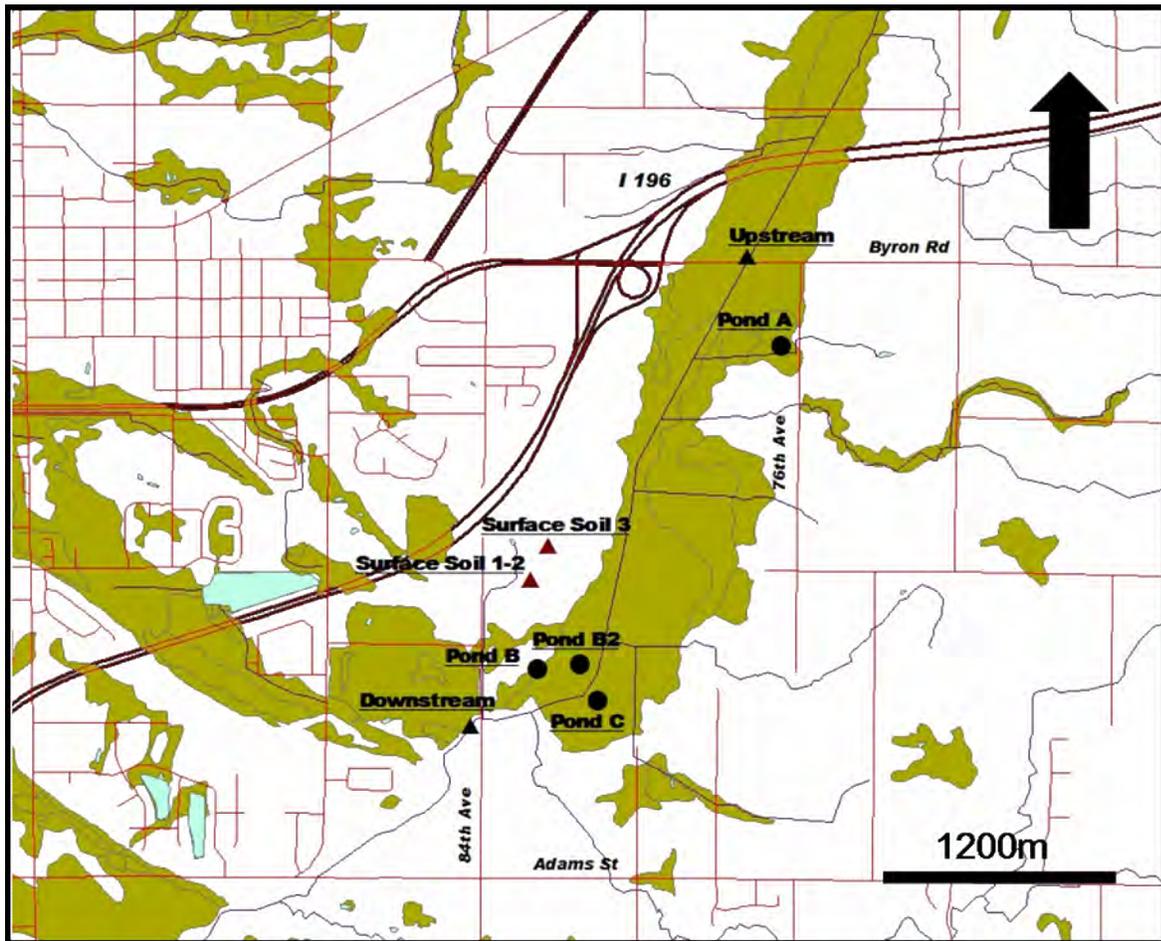


Figure 1. Map of Upper Mac Restoration site stretching from Byron Road and 76th Street down to 84th Avenue off of Adams Street.

The sampling site consisted of 8 total locations. Two of these were on the Macatawa River, four were from retention ponds within the Upper Mac Restoration area, and two were from highland locations adjacent to the restoration area. They were labeled by our group as

follows: Upstream (River), Downstream (River), Ponds A, B, B2, C and Surface Soil 1, 2, and 3 as seen in Figure 1. These sites were selected in order to provide a diverse range of geologic and hydrologic conditions.

The composition of sediment at each location varied. To begin, both the upstream and downstream river sites consisted of organic rich silt at the top followed by a fine–medium sand and finally, coarse sand at the bottom of the section. Pond A on the other hand was for the first 6 inches agricultural muck followed by a thick layer of dense gray colored clay overlaying more organic-rich agricultural sediment. Ponds B and B2 were mostly silty sediment followed by highly organic-rich sediment. Samples extracted from each location are as follows: **Upstream:** Water and Sediment; **Downstream:** Water; **Pond A:** Water and Sediment; **Pond B:** Water and Sediment; **Pond B2:** Sediment; **Pond C:** Water. **Surface Soils** were collected strictly from the highland ridges. These ridges were wooded, composed mainly of till and were mostly undisturbed. Ponds A and C were constructed in 2003 during Phase I Restoration and Ponds B and B2 were constructed in 2006 during Phase II.

METHODS:

Sampling. Samples had to be collected while avoiding contamination and they had to be correctly preserved in order to carry out proper chemical analysis. Water samples were collected in unused 500mL Nalgene[®] polyethylene sampling bottles. In order to collect the water, the bottles were attached to a 4.5 foot PVC pipe with a holster fastened to the end. Once full the bottles were capped and labeled, GPS coordinates were entered at each location and samples were stored on ice. The water was collected, brought back to the lab and acidified to 1% with concentrated TraceMetal Grade[®] nitric acid so as to prevent the precipitation of inorganic

phosphorus. Water was then stored in a refrigerator at 4 °C in the dark so as to slow down metabolism of phosphorus.

Sediment samples were collected in the field using a hand-held piston-corer composed of PVC. In order to obtain a core, a section of Lexan[®] tube is attached to the PVC pipe which is then driven perpendicularly into the sediment manually. The sediment is pulled into the Lexan tube through suction by pulling upwards on a cord that is looped out of the top of the PVC and that is attached to a plunger. Force is also exerted downward to drive the tube deeper into the stratified section. Once a core was obtained, suction was maintained and the core was pulled from the sediment. While still underwater, the Lexan[®] tube was capped with a rubber stopper. Cores were labeled and brought back to the lab. Surface soils were also collected from highland areas using 50 mL plastic centrifuge vials to scoop up the soil.

Sample preparation and analysis. All glassware and crucibles used with samples were cleaned with a 1:1 concentrated TraceMetal Grade[®] hydrochloric acid: de-ionized water mixture. For water preparation, samples were gravity filtered through 110 mm Whatman[®] Qualitative filter paper that had been rinsed with 1% concentrated TraceMetal Grade[®] nitric acid. This filtration removed any particulates from the water and samples were then ready for ICP analysis. Standards containing 25, 50, 100, 500, and 1000 ppb phosphorus were created and run along with the water samples.

When cores were brought back to the lab, if any water remained on the surface of the core, it was removed using a syringe and tubing. Cores were then frozen overnight or longer in order to preserve layering as they were extracted and to ensure that they remained in one piece. Before extraction, cores were thawed at room temperature for 1.5-4 hours. Sediment cores were then extruded with a ramrod and plastic disk. Once the cores were removed onto a clean stable

surface, pictures were taken for documentation of sediment layering and lengths were recorded and are presented in Table 1.

Location	Core length (cm)
Pond A	19
Pond B	20
Pond B2	20
Upstream River	38

Table 1. Length of cores from each site.

Crucibles were filled with samples taken from the top, middle, and bottom of each core and the samples were dried for five hours at 105°C to 115°C in order to drive off water (Note: Pond A and Upstream River samples were dried at 150°C). Half a gram of this dried sediment was weighed and placed in a microwave vessel along with 10 mL of concentrated TraceMetal Grade[®] nitric acid. The Microwave Accelerated Reaction System (MARS 5[®]) was used to digest the sediment, thereby leaching out any metals contained therein. Leachates were diluted to 50 mL and this was diluted another 10 fold and run through the ICP. Multi-elemental standards were run with the samples.

RESULTS:

Three sets of water samples were taken and analyzed in the month of October. An attempt was made to collect samples on dates when it was raining or had just rained. It was thought that runoff caused by rain would produce higher phosphorus concentrations in the ponds, which would give a greater chance of concentrations being above the limit of detection for phosphorus on the ICP (~30 ppb). Figure 2 shows precipitation data for October with the three sampling dates, the 2nd, 12th, and 27th, depicted as squares. None of the sampling times were on dates with significant rainfall. The USGS stream gauge on the Macatawa River read 2.5 ft, 2.5 ft, and 2.7 ft, respectively, for the sampling dates, indicating the river had elevated flow, yet not peak flow.

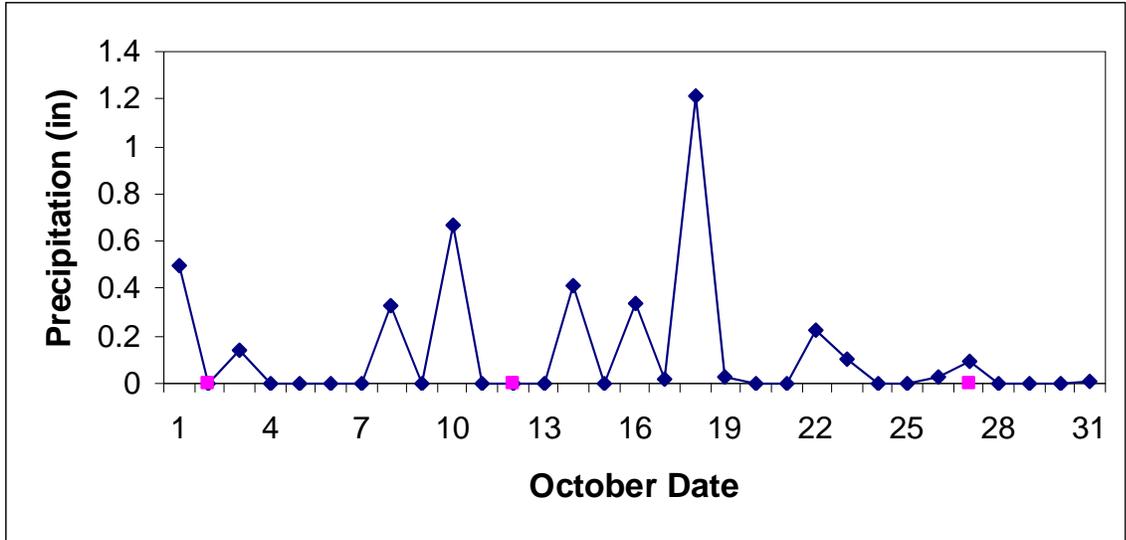


Figure 2. Precipitation in October with three sampling dates as squares.

The results of the water analyses are shown in Table 2 and graphically in Figure 3.

Uncertainties were calculated using standard analytical methods. Figure 3 contains a line that represents an average value (80 ppb) of total aqueous phosphorus levels for September of 2004 and 2005 at the USGS stream gauge site in the Macatawa River documented by the MDEQ (MDEQWB, 2004 and 2005). Because these results agree with the MDEQ data, the ICP method is valid.

Site	2-Oct [P] (ppb)	Error (ppb)	12-Oct [P] (ppb)	Error (ppb)	27-Oct [P] (ppb)	Error (ppb)
Pond A	128	30	190	10	121	18
Pond B	35	30	35	10	23	18
Pond C	175	30	160	10	101	18
Upstream	51	30	102	10	67	18
Downstream	93	30	89	10	78	18

Table 2. Phosphorus concentrations in water samples on three different dates.

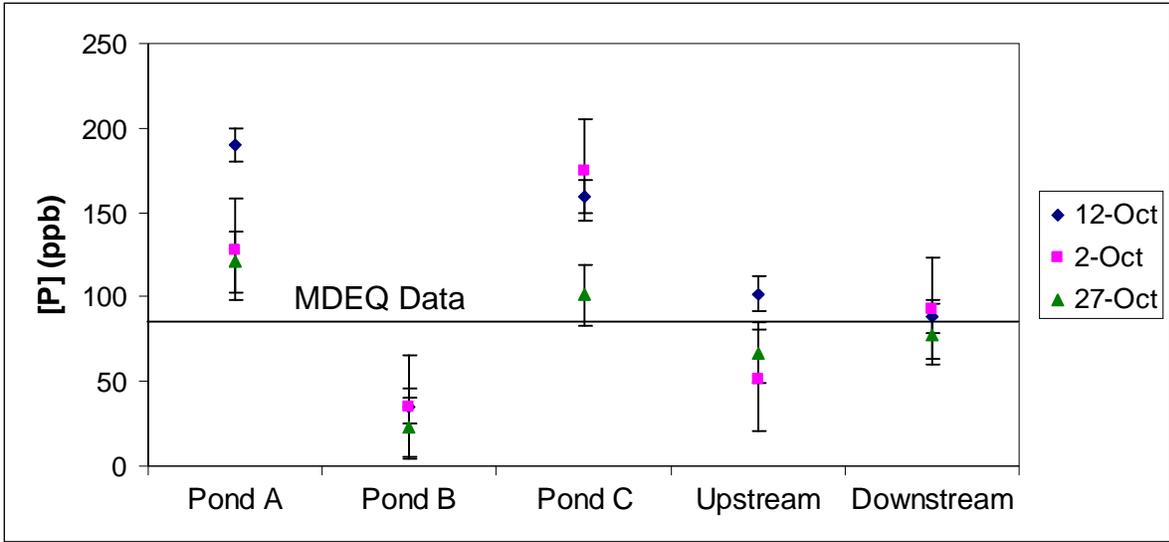


Figure 3. Phosphorus concentrations in water samples from the Upper Mac.

All sediment results are in Table 3. The samples were run with two sets of standards, one a multi-elemental standard with phosphorus added in, and the other with phosphorus only, since phosphorus has some interference on the ICP, which is explained in the discussion. Samples ending with A and B indicate replicates of the same sample in the same microwave digestion and ICP run. Samples labeled with an asterisk are replicates of the sample, but in separate microwave digestions/ ICP runs. Concentrations are acid-soluble orthophosphate and are in parts per million. A summary of the sediment core results is shown in Figure 4. The line in this case represents the average of three surface soil samples that were collected from the highland ridge in the Upper Mac.

Sample	[P] (ppm) (Multi-elemental standards)	[P] error (ppm)	[P] error %	[P] (ppm) (P-only standards)
Upstream 0-6 cm A	1020	31	3	1226
Upstream 0-6 cm B	1000	36	4	1201
Upstream 19-25 cm A	149	33	22	183
Upstream 19-25 cm B	153	14	9	188
Upstream 19-25 cm *	113	23	20	158
Upstream 36-38 cm A	42.8	25	59	56
Upstream 36-38 cm B	49.8	19	39	65
Pond A 0-3 cm A	421	26	6	508
Pond A 0-3 cm B	420	25	6	507
Pond A 7-9 cm A	334	8	2	404
Pond A 7-9 cm B	332	43	13	402
Pond A 7-9 cm *	255	10	4	385
Pond A 15-19 cm A	215	32	15	263
Pond A 15-19 cm B	265	26	10	321
Pond B 0 cm	467	24	5	723
Pond B 10 cm	278	20	7	422
Pond B 20 cm A	265	11	4	400
Pond B 20 cm B	253	26	10	382
Pond B2 0 cm	537	16	3	835
Pond B2 10 cm	212	25	12	316
Pond B2 20 cm	202	38	19	301
Soil 1A	248	35	14	374
Soil 1B	241	23	10	362
Soil 2	309	26	8	470
Soil 3	205	25	12	304

Table 3. ICP results from all sediment analyses.

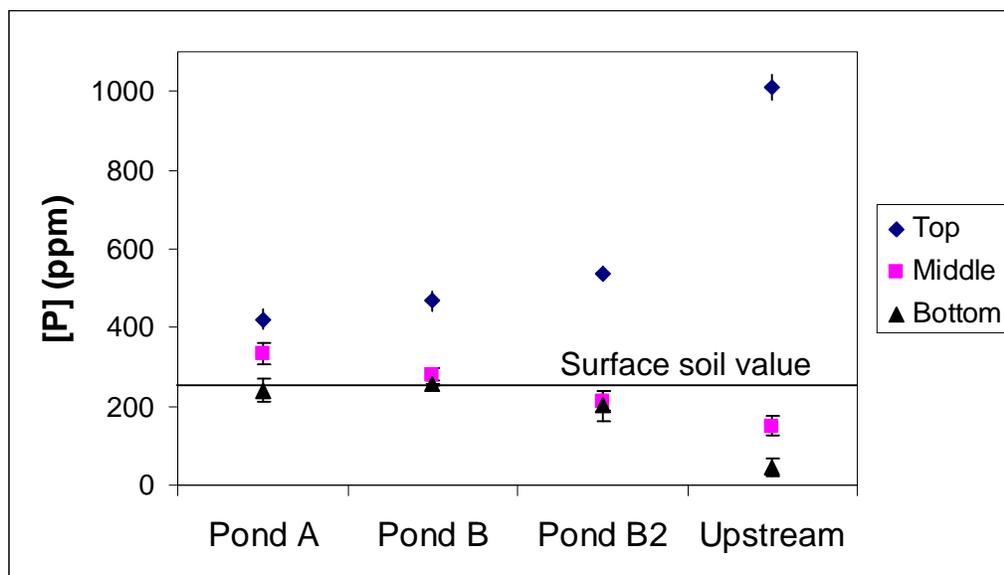


Figure 4. Orthophosphate concentrations in sediment cores from the Upper Mac.

DISCUSSION:

In general, the water concentrations between dates and sites do not show significant variance when the errors are taken into account. Pond B is significantly lower than either Pond A or Pond C, which could be due to the fact that the topography surrounding Pond B is fairly flat, unlike Pond A and Pond C. In addition, there are several other retention ponds near Pond B that may be collecting phosphorus that would otherwise be deposited into Pond B.

At every site, the top of the sediment core contains more phosphorus than the middle and bottom. The concentrations in the tops of the cores are also all greater than the surface soil samples. Both of these facts indicate that the ponds are accumulating phosphorus. The top layer of the Upstream River site is significantly greater than the ponds. Two explanations for this disparity are offered here. This phosphorus in the river could be historic phosphorus that has accumulated over the years from farm runoff and has remained in the sediment. It could also be an indication that the river has a source of phosphorus from farther upstream that is not shared with the ponds. However, phosphorus is a highly complicated element since it can adsorb to calcium, iron, and aluminum, and its form depends on pH and also redox conditions (Moore, 1991). The redox conditions may be different on the top layer of the sediment cores than in the bottom layers, which could cause a difference in phosphorus concentrations. But the concentrations on the top layers are still greater than those in the surface soils.

While the concentrations of phosphorus measured for water can be compared directly with previous measurements, the values presented for the sediment cores should not be taken as absolute. This means that the phosphorus concentrations presented here are not the exact concentrations in the sediment. One reason for this is that iron and aluminum cause background elevation for phosphorus on ICP, which makes phosphorus concentrations from the ICP lower

than their actual values (Varma, 1991). These sediment samples contain upwards of 10,000 ppm of iron and aluminum. An attempt to remove the iron and aluminum was made using a DOWEX[®] 50×2 strong acid cation exchange resin. This resin did not remove the iron and aluminum, however a different resin may be appropriate. Other techniques such as solid phase extraction could also be useful, but were not attempted in this experiment due to time constraints. Also, with the microwave digestion, only acid-soluble phosphorus is leached from the sediment. The National Institute of Standards and Technology 2586 Trace Elements in Soil Containing Lead from Paint standard yielded ~60% recovery of phosphorus.

Two separate microwave digestions and two separate ICP runs were completed for the sediment analysis. Pond A and the Upstream River sediment were one run and Pond B, Pond B2, and the surface soils were the second run. Different ranges of standards were used in each. The first run standards ranged from 10 ppb to 200 ppb and the second set ranged from 10 ppb to 10 ppm. However, these standards are multi-elemental containing iron, aluminum, copper, as well as other metals and phosphorus added in. Since copper interferes with phosphorus, this could have affected the calibration for phosphorus.

Standards containing only phosphorus were also run ranging from 10 ppb to 10 ppm. Concentrations determined from the phosphorus-only standards were on average 23% higher than the multi-elemental standards in the first run and 50% higher in the second run, as seen in Table 3. This difference in percentage is thought to be due to the varied range of multi-elemental standards used. This does not affect comparisons made within the cores themselves, but could possibly affect comparisons between sites. Keeping this in mind, it should not be concluded that phosphorus concentrations in Pond A, Pond B, and Pond B2 are different, but the level of phosphorus in the Upstream River site is almost definitely higher than the ponds.

Referencing Table 3, replicates ending with A and B agree to each other to within 5% with the multi-elemental standards and they vary up to 22% with the phosphorus-only standards. The replicates between the two digestions/ICP analyses marked with an asterisk vary up to 26% with the multi-elemental standards and up to 24% with the phosphorus-only standards.

CONCLUSIONS:

Pond B contains lower phosphorus levels in the water than Pond A and Pond C, which is due to the surrounding flat topography and other nearby ponds collecting phosphorus. Besides this, no significant differences in phosphorus concentrations in the water exist between sites, but values generally agree with previous MDEQ testing.

In comparison to the concentrations of phosphorus found on the surface of the pond cores, the river has a higher surface concentration of phosphorus, which is either due to historic events or a source of phosphorus that is not directly connected to the ponds. Decreasing phosphorus concentrations with depth was seen in sediment cores. In addition, surface values of phosphorus in the cores exceeded that of surface samples taken from undisturbed areas. These trends in the cores indicate that phosphorus accumulation is beginning to occur in the retention ponds.

Further testing would need to be completed in order to determine the exact effect of iron, aluminum, and copper on the phosphorus concentrations from the ICP. Other parameters worth testing may also be soil and water pH, total organic content of the sediment and additional sediment cores should be taken in order to confirm results presented here. Overall, this study serves as a foundation to future testing of the Upper Mac Restoration.

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