Final Report – Determining Components for a Phosphorus Interceptor to Reduce Harmful Algal Blooms in the Western Lake Erie Basin. PI – Daryl F. Dwyer, Ph.D., Department of Environmental Sciences, The University of Toledo, Toledo, OH.

1.a. Problem and Research Objectives - Harmful algal blooms (HABs) have been observed annually in the western Lake Erie basin since the mid-1990s; some of the most extensive blooms were observed in recent years (Bridgeman et al., 2012; Michalak et al., 2013). HABs are due to complex interactions among multiple factors that may include nutrient input from agricultural fields, climate change-induced increases in temperature and in the frequency and severity of storms, and the unique geomorphology of Lake Erie, which is shallow and warm (Michalak et al., 2013; Smith et al., 2015). HABs in Lake Erie appear closely linked to agricultural nutrients, specifically nitrogen (N) and soluble phosphorus (SP) (Chaffin et al., 2011; Bridgeman et al., 2012). An estimated 50% of the total phosphorus (TP) loading to Lake Erie is derived from the Maumee River (Dolan and McGunagle, 2005) with 49% from agricultural sources (Robertson and Saad, 2011). Studies indicate (Smith et al., 2015) that approximately 50% of phosphorous emissions may be derived from subsurface tiles, which suggests that tile drainage is equally as important as surface runoff. Unfortunately, tile drainage has been overlooked by the traditional best management practices (BMPs) implemented by agricultural conservation programs that focus on management and reduction of nutrient transport as surface runoff (Sharpley et al., 2006). Therefore, we proposed to develop a "nutrient interceptor" to harvest phosphorus from agricultural-derived water emitted via drainage tiles.

The proposed nutrient interceptor is a simple, easy to install device that can be implemented throughout the Maumee River watershed and is basically a surface container filled with mesh bags of replaceable filter media with the appropriate properties to adsorb SP. We previously evaluated several types of filter media including commercial sorbents, biochar, and mussel shells, which proved to be the best sorbent with an average 13% reduction in SP. We proposed to evaluate additional types of natural filter media, including locally-derived limestone, for comparison with the initial results. The sorbent with the highest SP removal was to be field tested in nutrient interceptors stationed at farm fields within the Wolf Creek watershed to test the efficiency of SP-removal. Thus, for this project, three specific objectives were created: (1) determine the most appropriate filter media and hydraulic retention time for P nutrient interceptors, (2) investigate rain event-based P loadings from agricultural fields, and (3) quantify the reduction in P using the nutrient interceptors.

Unfortunately, the field work portion of the project was not successful due to two factors: (1) the drain tile mains were below the water level in the ditches into which they emptied during rain storms that occurred after fertilization of the farms fields. Thus, we were unable to place the interceptors into position. (2) When the water levels were low enough to access the drain tile mains, fertilizer had not been applied to the fields. To substitute for the field work, we brought the drainage water to the laboratory, added phosphorous to attain concentrations relevant to those observed in the field, and set up the nutrient interceptors in the laboratory for testing their effect on this amended water.

1.b. Methodology

PSM characterization. The selection of a phosphorous-sorbing material (PSM) was prefaced on availability, cost, and performance. Three materials that were both readily available and inexpensive were chosen for comparison with respect to performance – each of the test materials (water treatment plant residuals, quarry-derived limestone, and crushed zebra mussel shells) was calcium-based; sand was used as a control. Water treatment plant residuals were acquired from the Toledo Water Treatment Plant, ground and passed through a sieve to obtain sizes less than 850 um. Limestone gravel was obtained from a local quarry. Zebra mussel shells were obtained from the shoreline of Lake Erie, passed through a series of three sieves to obtain fractions of the following sizes: < 850 um; 850 um to 2 mm; 2mm and 4mm. Each material (including all three size fractions of zebra mussel shells) was characterized (Lyngsie et. al, 2015) in triplicate as follows: (i) Bulk Density. PSM (100 cm^3) was weighed and the density calculated. (ii) Porosity. PSM (40 cm^3) was saturated with DI water within a graduated cylinder and the volume divided by the measured quantity of water. (iii) pH Bench Test. PSM (15 g) was added to DI water (150 mL) and to Maumee River water (150 mL) in 250 mL Erlenmeyer flasks; pH was measured using a Toledo Mettler Seven Go Pro.

Rates of phosphorus adsorption. PSM (2 g) was placed into solutions (30 mL) containing known concentrations of SP (0.5, 1.0, 5.0, 10 and 25 mg P/L). The stock solution of SP was made by dissolving 0.2129 g of KH_2PO_4 into 1 L of 18-ohm reverse osmosis filtered water, resulting in a solution of 50 mg P/L. In the initial experiments, to maintain a controlled experimental setting, the 30 ml of solution was modified Hoagland's solution containing per liter, 0.0379 g of K_2SO_4, 0.0254 g of NaCl, 0.0568 g of $MgSO_4$, and 0.448 g of $CuSO_4$. This solution approximated the nutrient composition of the Maumee River. Each setup was done in triplicate and placed on a bench shaker; water samples (1 mL) were taken at 1, 10, 30, 60 min, 5 and 24 hours after shaking (120 rpm) commenced, centrifuged to remove solids, and tested (EPA method 365.2, Rice et al., 2012) for PO_4^{-3} and reported as mg P/L adsorbed to each PSM.

Phosphorous sorption capacity. Water treatment plant residuals were selected for further experimentation based on the initial analysis. Samples (5 g) were mixed evenly with laboratory grade sand (95 g) and placed into six PVC columns (3.8 cm diameter by 20 cm height) in triplicate (Figure 1). A 45-um filter was added to the bottom of each column to prevent PSM from passing into collection flasks. Phosphorus solution (1 mg P/L) was added to each column with constant head pressure, allowed to percolate through the PSM mixture and effluent samples collected every 30 min for 5 hr. Samples were then analyzed for SP.

Figure 1. Experimental setup to determine the phosphorous sorption capacity of water treatment plant residuals.

Efficacy of the nutrient interceptor. The nutrient interceptor (Figure 2) was constructed using two 19 L open top buckets, two 1.27 cm diameter bulkhead fittings, and a 5-micron industrial filter. Tile drainage water from a farm field (located in Oregon, OH) was amended with the stock P-solution to attain a concentration of 2.5 mg P per liter. The water was first tested to ascertain that the field water did not alter the sorption efficiency or capacity of the nutrient interceptor. The interceptor contained water treatment plant residual (18% by weight) mixed with sand to a final mass of 3 kg. Water (40 L) was gravity fed through the interceptor using a 2 meter head at a rate of 3 liters per minute. Water samples (10 mL) from the inflow and outflow of the interceptor were taken over time until the water was depleted.
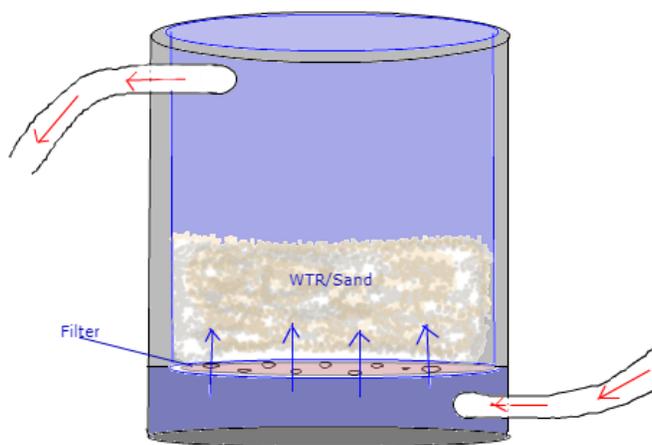

Figure 2. Diagram of the nutrient interceptor designed to test the phosphorous-removal efficacy of the water treatment plant residuals. A photograph of the system in the laboratory is provided with this report.

1.c. Principal Findings and Results

Rates of phosphorous adsorption. Over a period of 24 hours, the amount of phosphorous adsorbed to each PSM increased (Figure 3). The water treatment plant residuals demonstrated the relatively quickest sorption for each tested concentration – sorption was complete within 1 minute when compared to the slower rates for the remaining PSMs. For this reason, water treatment plant residuals were selected for further testing.

Figure 3. The quantity of phosphorus adsorbed by each PSM over a 24-hour period. The most rapid adsorption rate occurred with the water treatment plant residuals.
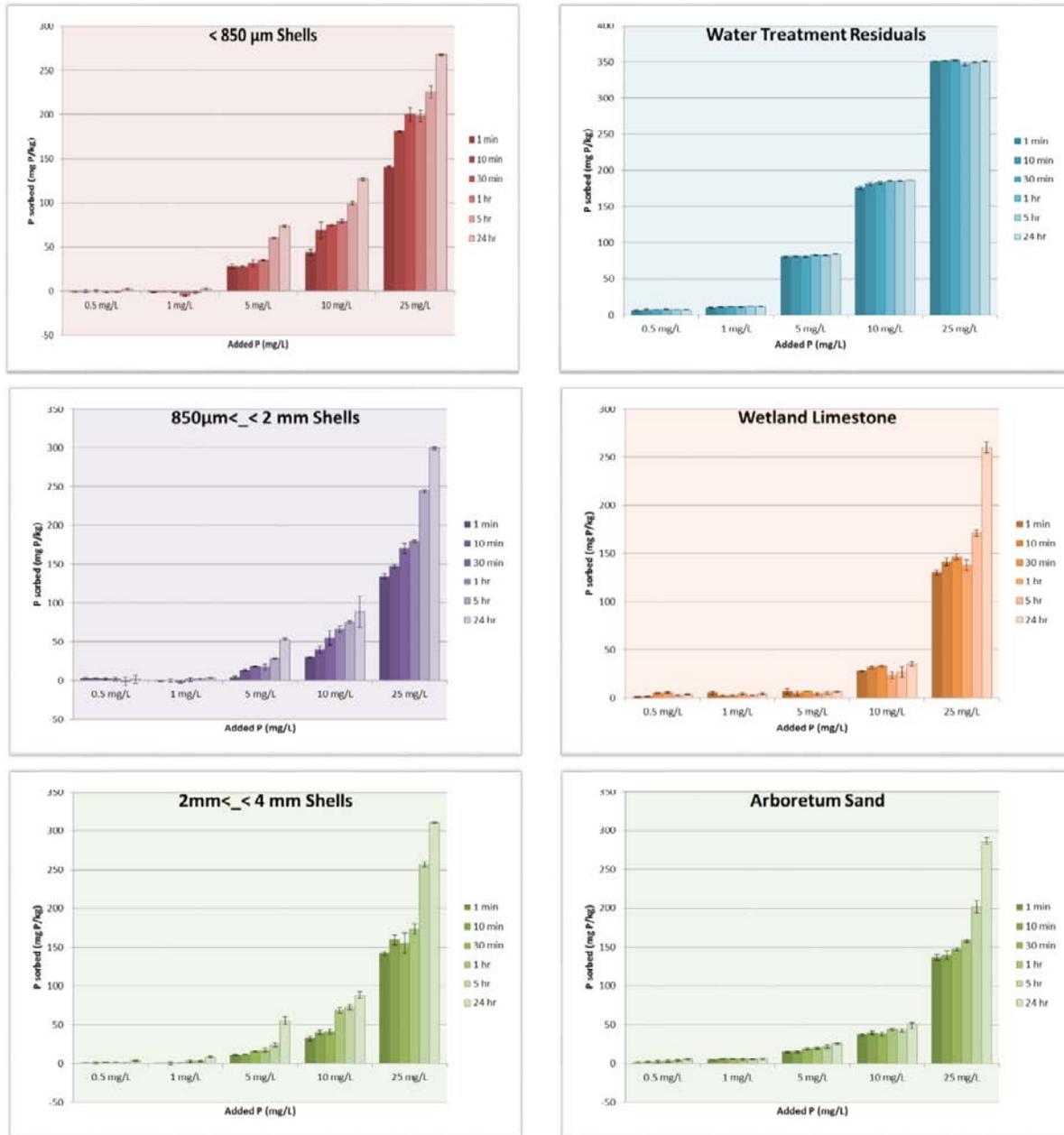
Phosphorous sorption capacity. Data for each experimental trial – using sand as a control and the water treatment plant residuals - is provided in Figure 4. The amount of phosphorous adsorbed by sand decreased over time, which is an anomaly that may be explained only if the sand had attached phosphorous that was released. More noteworthy are the results using water treatment plant residuals to which P adsorbed over the 300-minute trial. Note that compared to the batch systems, in which adsorption occurred almost instantaneously, the flow through systems used in these experiments allowed for continuous removal of phosphorous over time, but did attain what appears to be saturation of the PSM.
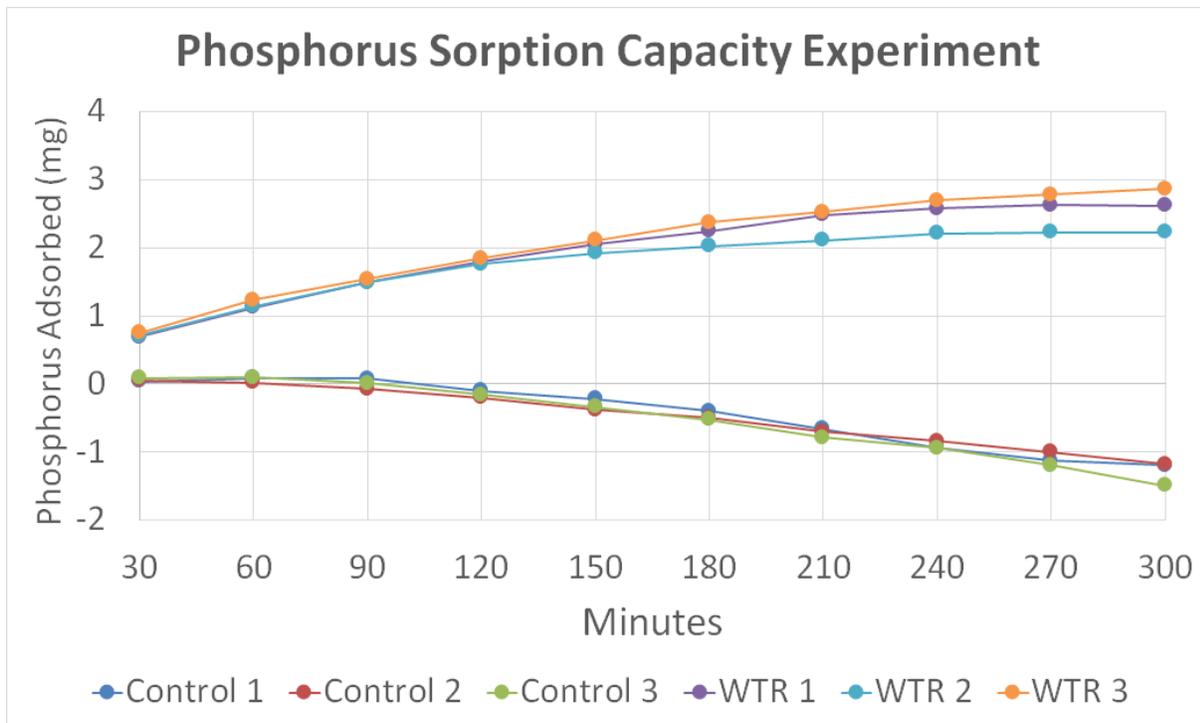
Figure 4. The sorption of phosphorous in flow-through systems occurred continuously over time and leveled-off near the end of the 5-hour experiment, presumably due to saturation of the PSM.

Efficacy of the nutrient interceptor. The nutrient interceptor (Figure 5) had farm field water to which phosphorous had been amended passed passed through and samples of water analyzed to determine the amount of adsorbed phosphorous with the data presented as both the reduction in concentration of P and percentage of P. Initially, reductions of 15% occurred, but this percentage decreased to 10% as the PSM, presumably, became saturated.

Figure 5. Average reduction of phosphorus (mg/L; red line) and average percent reduction of phosphorus (%; blue line) of spiked tile drainage water (2.5 mg P/L) calculated for each effluent sample for the nutrient interceptor (NI) trials. Discrete phosphorus reduction decreases indicating the gradual tendency to saturation of the WTR.
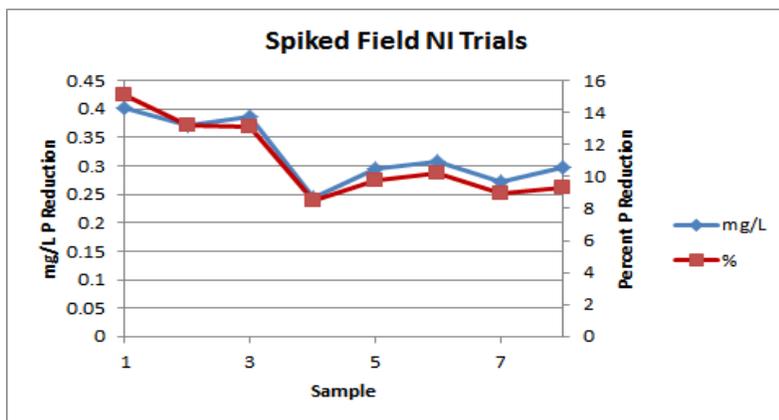
1.d. Finding Significance. The water treatment plant residuals worked relatively well within the scope of this project, especially when compared to other potential PSM material. We are currently continuing with this project to formulate the residuals into a material that can be used in large scale nutrient interceptors. Interest in media that can be used to remove nutrients from agricultural field water is not new. However, the results here demonstrate that a waste product from water treatment plants can function as a PSM. It is worth noting that the City of Toledo currently spends millions of dollars each year to dispose of the residuals. Conversion to a PSM instead of disposal would potentially save municipalities money and create a product that can be used to improve water quality.

1.e. Literature Cited

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