MDARD Horticulture Fund Project Title: Efficiency of Bioreactor Nutrient Remediation in the Presence of the Organophosphate Chlorpyrifos

2017 1st year Report

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The focus of this study was to quantify if, and to what extent, certain classes of pesticides threaten agricultural runoff treatments, such as bioreactors. Simulated runoff was created using organophosphate Chlorpyrifos along with nitrate and phosphate, the primary nutrients responsible for eutrophication. Two chamber bioreactors comprised of two distinct processes were constructed. The first chamber was a woodchip bioreactor used to reduce nitrate levels and bind and/or degrade pesticides. The second chamber relied on using calcined aggregates, specifically haydite, a shale product, and turface, a clay product, to adsorb phosphorus.

The first round of this study was conducted from 27 January to 9 June 2017 with a second round planned for the winter of 2017-2018. Throughout the first 13 weeks of the study, all 20 of the bioreactors were supplied with the same influent comprised of a potassium nitrate and potassium monophosphate solution injected into the influent line, resulting in 20 $mg \cdot L^{-1}$ NO_3^- and 4 $mg \cdot L^{-1}$ PO_4^{3-}. Starting on 18 April, chlorpyrifos (as Lorbsan 4E) was incorporated into the influent solution provided to half of the bioreactors at a concentration of 1 $mg \cdot L^{-1}$ via the use of a second injector. Throughout the experiment, four gallons of influent were supplied daily to each bioreactor. Weekly water samples were collected from the outlets of all bioreactor chambers. The pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) levels of the water samples were measured immediately after collection, after which the samples were frozen for later nutrient and pesticide analysis.

The pH of the woodchip bioreactors was usually slightly lower than the cacined aggregate bioreactors within the same chlorpyrifos treatment. After the incorporation of chlorpyrifos, the substrate pH of the bioreactors receiving chlorpyrifos initially were slightly higher than their respective

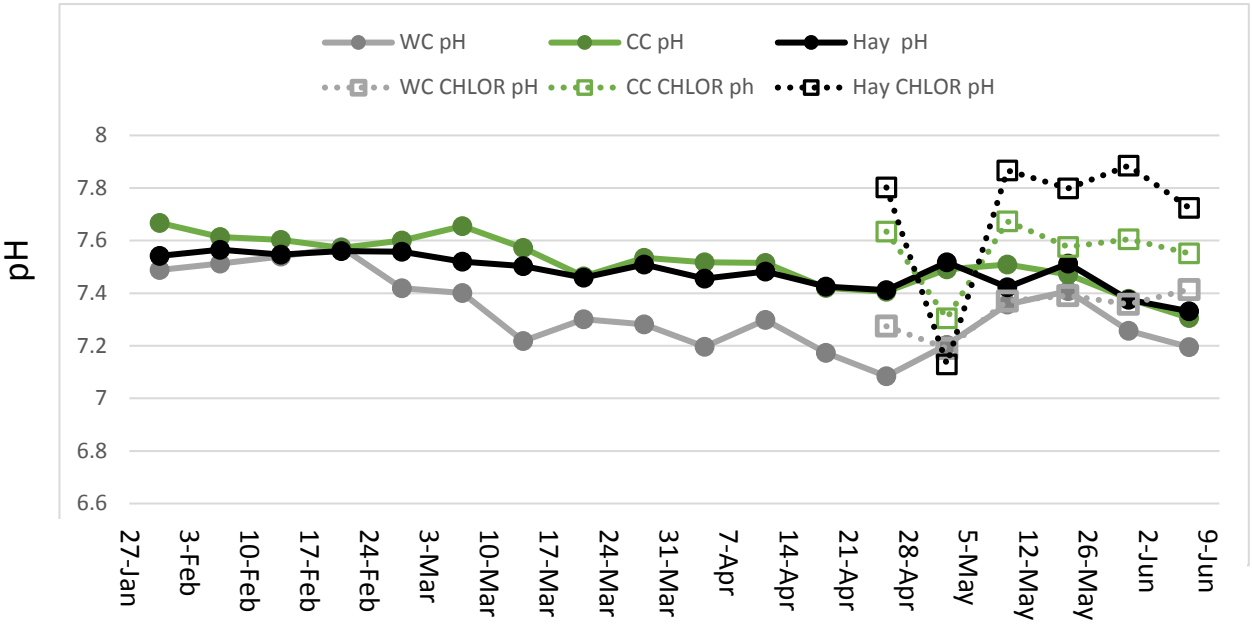

Figure 1. Bioreactor substrate pH in 2017 before and after addition of chlorpyrifos to simulated nursery runoff water. WC = woodchip, CC = calcined clay, Hay = haydite; solid lines with solid circles represent bioreactors that did not receive chlorpyrifos, dotted lines with open squares represent bioreactors that received chlorpyrifos. Bioreactors treatments with nitrate and phosphate enriched water began on January 27 and ended on June 9. Chlorpyrifos was added to half of the bioreactors from April 18 to June 9.

controls (the same substrate without chlorpyrifos) followed by a slight depression in pH and then a slight increase again (Figure 1). The opposite response was seen for ORP measurements, ORP was typically highest for the woodchip bioreactors within the same chlorpyrifos treatment and the chlorpyrifos treated bioreactors initially were lower immediately after chlorpyrifos incorporation than their respective controls then slightly higher before becoming lower for the calcined aggregates for final three weeks (Figure 2). Differences in DO were minimal (Figure 3). Statistical analysis remains to be conducted to determine if any of these differences are significant.

Pesticide and nutrient sample analysis is underway, which will quantify how incorporation of chlorpyrifos in amounts expected to be found in nursery runoff may change the population of

microorganisms that may be involved in nutrient and pesticide remediation, as well as the potential to compete for binding sites on the calcined aggregates. The effluent nutrient and pesticide concentrations will also assist in quantifying the serviceable lifespan of the adsorptive aggregates we used, enhancing the decision support system needed to maintain bioreactors.

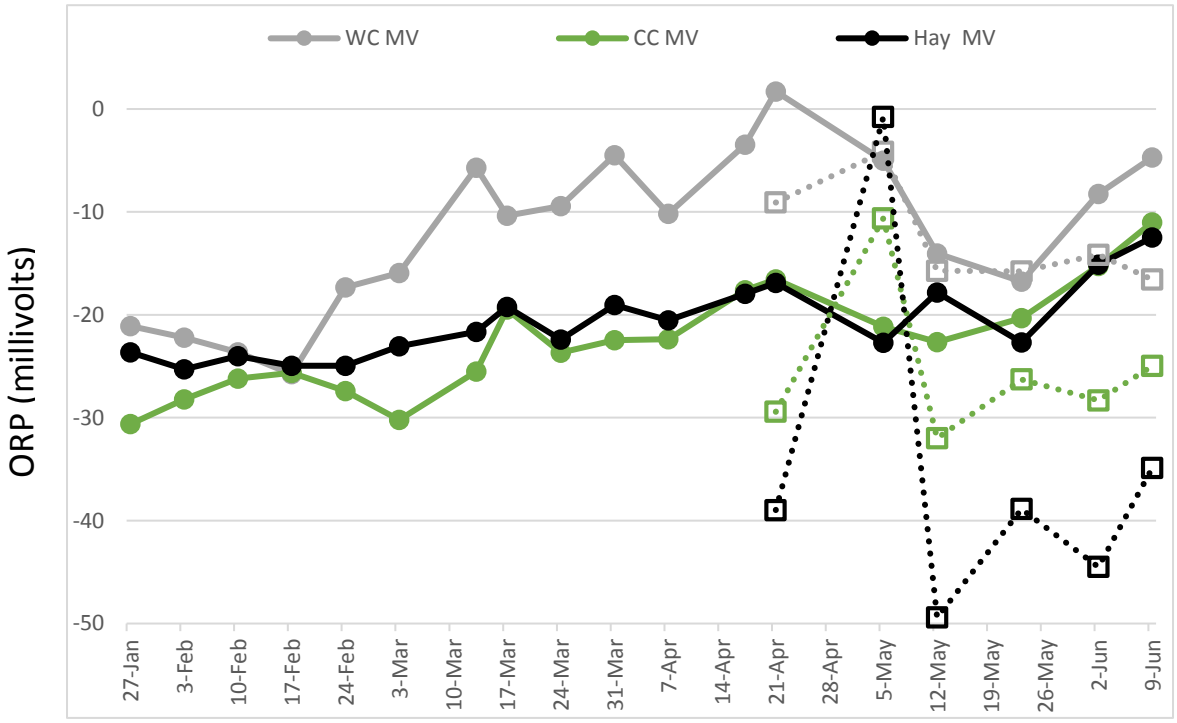

Figure 2. Bioreactor substrate oxidation-reduction potential (ORP) in 2017 before and after addition of chlorpyrifos to simulated nursery runoff water. WC = woodchip, CC = calcined clay, Hay = haydite; solid lines with solid circles represent bioreactors that did not receive chlorpyrifos, dotted lines with open squares represent bioreactors that received chlorpyrifos. Bioreactors treatments with nitrate and phosphate enriched water began on January 27 and ended on June 9. Chlorpyrifos was added to half of the bioreactors from April 18 to June 9.

Initial samples of the microbial communities in the woodchip bioreactors prior to chlorpyrifos injection have been isolated via polymerase chain reaction and electrophoresis and will be compared to microbial samples harvested at termination of the study currently to determine the effects of chlorpyrifos on the microbial community and if a shift in microbial species developed. Such a shift may result in identification of organisms capable of tolerating and degrading chlorpyrifos and other pesticides.

At the conclusion of year one of this study, we have been able to quantify materials for their potential to be used for agricultural runoff treatment, derive methods for the analysis of microbial communities found in woodchip bioreactors, and improve our knowledge of chlorpyrifos partitioning throughout the treatment system. Once final nutrient and pesticide results are analyzed and DNA is sequenced, we can more effectively answer if small amounts of chlorpyrifos cause changes to the treatment efficacy and the microbial communities present. Based on data generated in year 1, we will refine our treatments in order to better determine the fate of agrichemical inputs to the system, enhance treatment material knowledge and selection, and to further efforts to make sustainable agricultural water treatments achievable.

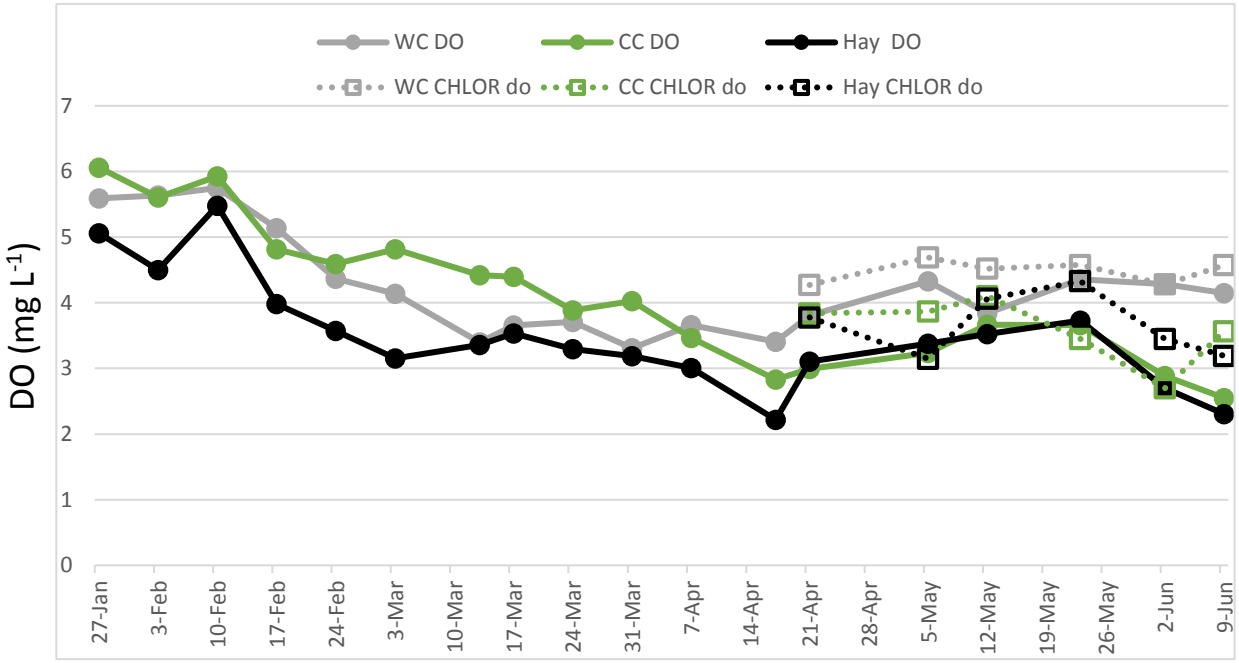

Figure 3. Bioreactor substrate dissolved oxygen (DO) content before and after addition of chlorpyrifos to simulated nursery runoff water. WC = woodchip, CC = calcined clay, Hay = haydite; solid lines with solid circles represent bioreactors that did not receive chlorpyrifos, dotted lines with open squares represent bioreactors that received chlorpyrifos. Bioreactors treatments with nitrate and phosphate enriched water began on January 27 and ended on June 9. Chlorpyrifos was added to half of the bioreactors from April 18 to June 9.