

Thank you to Jasmine Schneider for the use of her CWSF 2022 project as an example of the template. This a design example and not a direct copy of the project.

Adding mussel shells to biochar resulted in capturing 80% of phosphate from water, reducing a cause of algae blooms.

Why?

Eutrophication, the addition of excess nutrients (especially phosphate) to a body of water resulting in increased algal growth, is considered to be one of the leading contributors to the deterioration of aquatic ecosystems. One potential method to remove phosphate from water is through the use of biochar, a carbon-rich material produced via thermal decomposition (pyrolysis) that can be derived from any number of different organic waste products (feedstocks).

Notably, when it comes to phosphate, the elemental composition of the feedstock is extremely important as the main mechanism for sorption in biochars has been found to be chemical precipitation often via calcium or magnesium ions.

This study is looking at five different locally accessible feedstock types: pumpkin vines donated by Shantz Family Farm, grape vines, dandelions, Waterloo's municipal compost, and municipal yard waste. Eddo peels sourced from the grocery store were also studied. These feedstocks were chosen as they are all considered waste products and they do not have any prior research on their ability as biochar to remove phosphate. The effect of adding mussel shell powder to the feedstocks before pyrolysis will also be tested.



How?

- All feedstocks were air dried for 14 days, before packed into cans. Placed in propane barbecue, temp. increased slowly to maximum treatment temp. of 400 °C.
- Feedstocks kept inside the barbecue for 3 hours total. Once removed, the biochar was crushed and then sieved using a 2 mm sieve to remove any finer fractions.
- Biochars individually mixed with groundwater (1:75 ratio), shaken for 24 hours to identify the amount and type of contaminants leaching from biochars (leachate test).
- Analysis performed for pH, phosphate, and ammonia using a pH meter, HACH orthophosphate reagent kit, and HACH ammonia kit respectively. The samples' dissolved organic carbon and inorganic carbon levels, as well as the concentrations of various elements were also analyzed.
- From this data, the four feedstock types that had the lowest amount of phosphate leaching were selected: grape vine, pumpkin vine, compost, and yard waste.
- Samples of these feedstocks were then pyrolyzed with the addition of mussel shell powder at a concentration of 1:2, mussel shell to feedstock (i.e. modified biochars).
- All samples were put through another leachate test as described above.
- Grape vine, the feedstock that had the least leaching with mussel shell powder proceeded to the actual phosphate removal test.
- Samples of modified grape vine biochar with a 1:2 and a 1:1 ratio of mussel shell to feedstock were both tested. The modified grape vine biochars added at a 1:75 ratio to groundwater that had been spiked with phosphate solution. Samples were placed on the shaker for 24 hours. Same day analysis was then performed for phosphate.

So What?

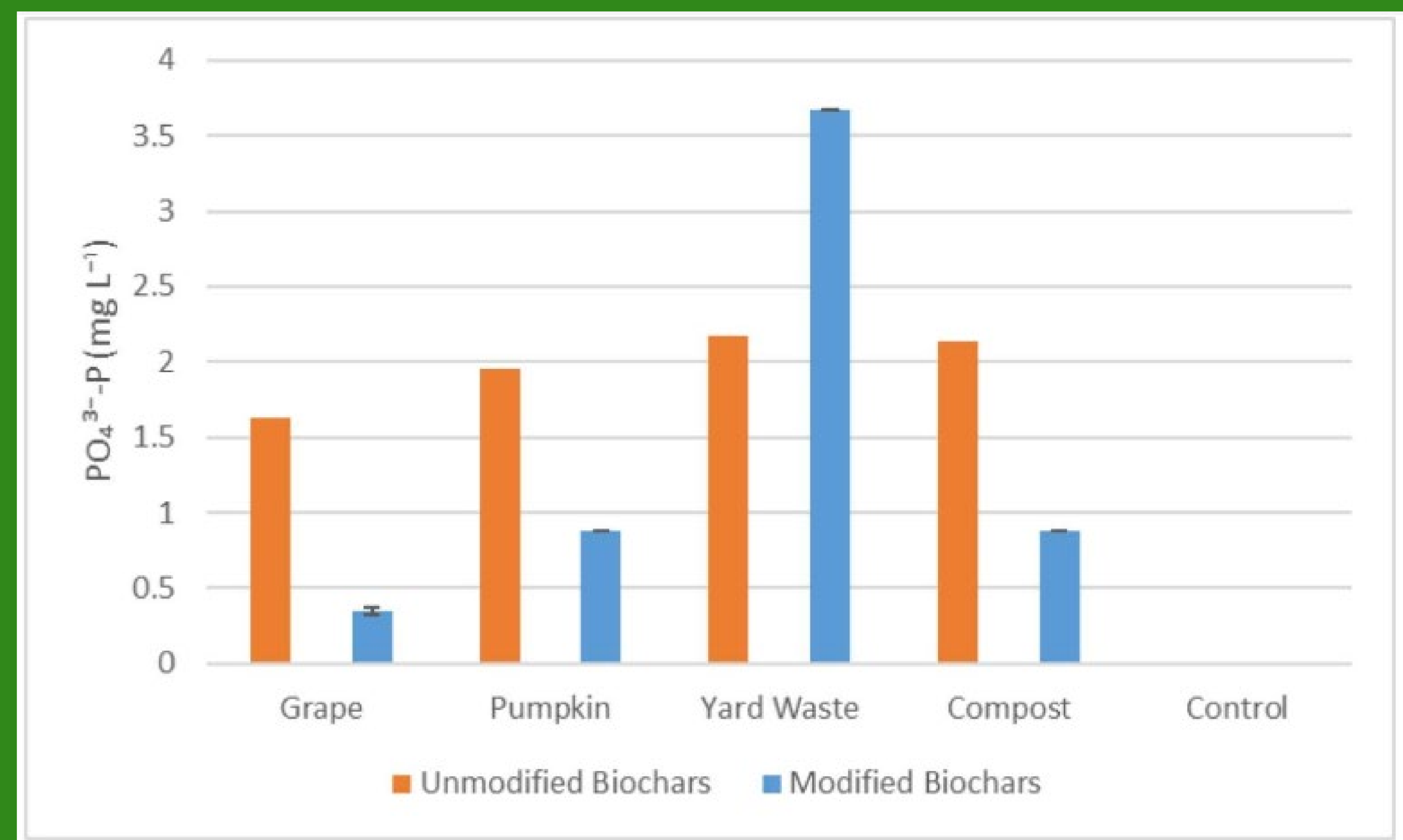
Although phosphate removal was not achieved with the current biochars, mussel shell powder as an effective and environmentally friendly way to load calcium onto biochars does show promise. Many of the studies that have gotten their respective feedstocks to the point of removal employ multiple modification methods; combinations of mussel shell and other enhancements may be explored in future research. The roughly five times reduction in phosphate leaching suggests that mussel shell could feasibly supplement the chemical reagents currently most commonly used for biochar calcium-doping. It should be considered that if a higher pyrolysis temperature were available, the calcium carbonate may have thermally decomposed more, potentially increasing the calcium load onto the biochars.

This is not only applicable to biochar as an adsorbent, but also as a soil amendment. Some biochars have been shown to improve soil pH and nitrogen fertilizer-use efficiency, but they have been found to result in additional phosphate leaching in column tests as well as in the current study. Mussel shells could be a valuable addition to biochars used for soil amendment purposes, as the observed reduction in initial phosphate leaching may translate to a slower release soil conditioner. This would be especially beneficial for preventing eutrophication when biochar is used to ameliorate abandoned mine land soil, or other instances where it would be applied in large amounts to soil.

Finally, the biochar's seemingly already effective ability to remove copper from water suggests that it might make a good material for dealing with copper contamination.

What?

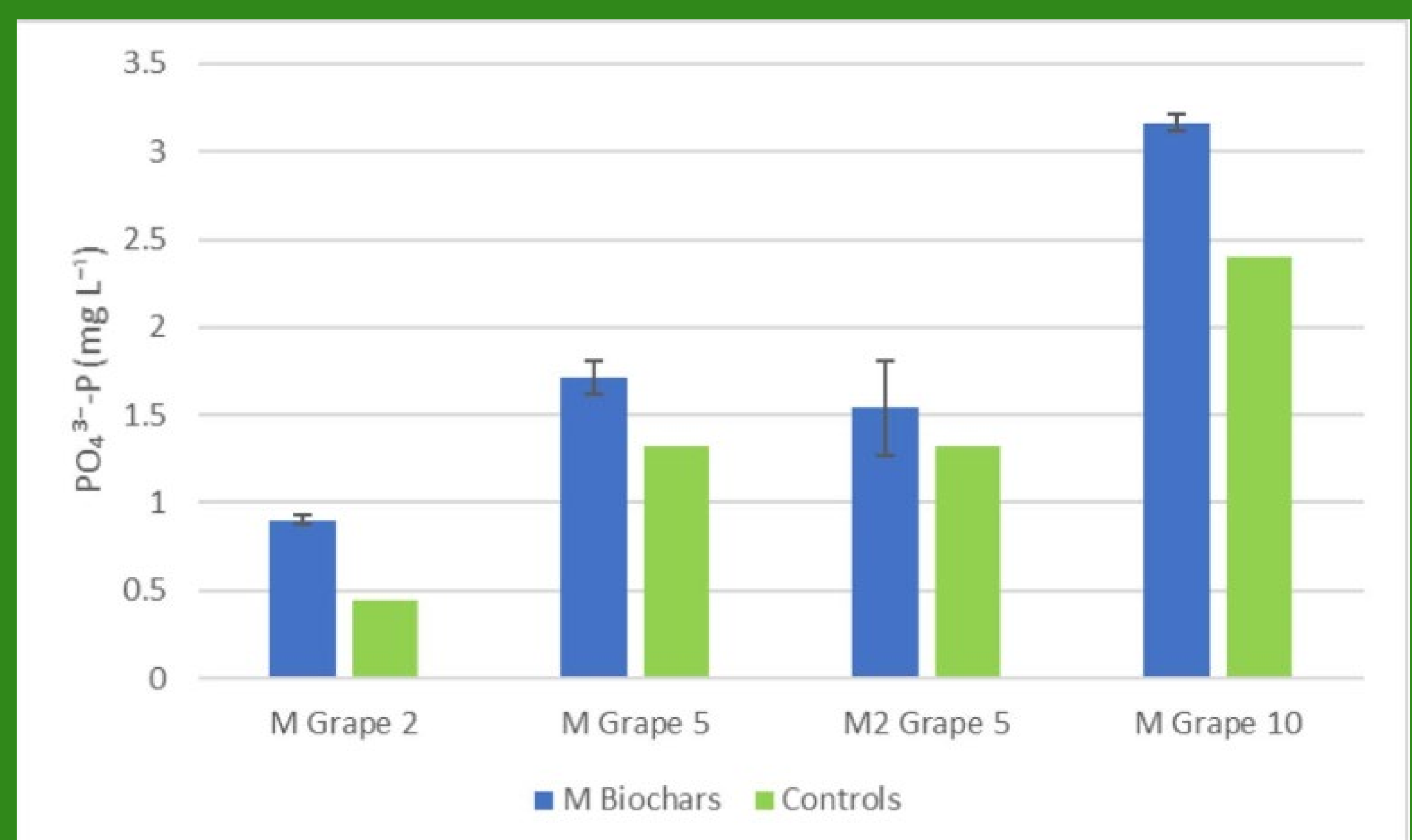
Figure 1: Grape vine biochar had the highest reduction in phosphate leaching with phosphate levels decreasing by approximately 80% after being modified



The first leaching test with unmodified biochars showed that all feedstock types resulted in at least 5 mg/L additional phosphate leaching. The grape vine biochar had the least amount of phosphate leaching, followed by pumpkin vines, then compost, then yard waste; all leached less than 7 mg/L. Eddo peels and dandelion leaves showed the most phosphate leaching by a significant margin; both had phosphate concentrations between 49-65 mg/L.

Next came the leaching test with modified biochars. When those results were compared to the leaching test with unmodified biochars, it was observed that most of the biochars had a significant reduction in phosphate leaching after being treated with mussel shell powder. Yard waste biochar was an anomaly, but this is likely due to its inherently variable composition. Some samples of yard waste may have contained more leafy material than others; it was observed in the first leaching test that dandelion leaves leached much more additional phosphate than the other feedstock types. Overall, across most key analyses, grape vine biochar tended to have the least leaching of contaminants, with a lower release of ammonia, dissolved organic carbon, and potassium when compared to the other feedstocks.

Figure 2: The lowest amount of phosphate leaching obtained was a mean of 0.22 mg/L from the biochar modified with a 1:1 ratio of feedstock to mussel shell (Figure 2)



As indicated in the leachate tests, even when modified the grape vine biochar was still unable to remove phosphate in the removal test, and the lowest amount of phosphate leaching obtained was a mean of 0.22 mg/L from the biochar modified with a 1:1 ratio of feedstock to mussel shell (Figure 2). However, cation measurements from the leachate tests did show significant removal of copper. The blanks had a mean copper concentration of 2573 µg/L, which is well over the maximum contaminant level recommend by the EPA: 1300 µg/L, whereas the leachate sample from yard waste biochar in particular had a mean copper concentration of 150.45 µg/L, representing approximately a 94% reduction.

What's next?

One possible route for the future of this project is to try to get the biochars to a point of phosphate removal by adding a secondary modification method alongside the mussel shell. Water softener backwash for example, is high in iron, another element that can aid in the removal of phosphate. Soaking the feedstocks in the water softener backwash might be another helpful and resourceful way to modify biochars.

Further research may also look at different properties of the biochars, such as their ability to remove heavy metals, especially seeing as they have already shown great potential in copper removal.



References and Thanks

Thanks
I would like to thank Dr. Carol J. Ptacek for providing me safe access to her lab, and for taking the time to share her knowledge on biochar as well as to answer my many questions. I am also very grateful that she offered to run my samples through the ICP and IC, as funded by her research group's student grant. Additionally, many thanks are due to Sara Felling, lab technician, for training me on how to use the required lab equipment, and for supervising me the entire time I was in the lab. Credit goes to Shantiz Family Farm for letting me collect pumpkin vines from their fields, and to Thomas Oakman for providing samples of Waterloo's compost. Last but not least, I would like to recognize the efforts of my parents, especially seeing as they very graciously allowed me to air-dry municipal compost in our shed.

Journal Articles:
Almanassra, I. W., McKay, G., Kochkodan, V., Ali Atteh, M., & Al-Ansari, T. (2021). A state of the art review on phosphate removal from water by biochars. *Chemical Engineering Journal*, 409, 128211. <https://doi.org/10.1016/j.cej.2020.128211>
Dincer, I., & Abu-Rayash, A. (2020). Sustainability Modeling. *Energy Sustainability*, 119–164. <https://doi.org/10.1016/b978-0-12-819556-7.00006-1>
Domagalski, J. L., & Johnson, Henry. 2012. *Phosphorus and Groundwater: Establishing Links Between Agricultural Use and Transport to Streams*. U.S. Geological Survey Fact Sheet 2012-3004, 4 p.
Dorley, L. K. (2015). *Slow pyrolysis biochar from forestry residue and municipal and farm wastes: Characterization and their use in greenhouses as a soil amendment*. MSc Thesis. Environmental Science. Memorial University of Newfoundland, St. John's, NL, Canada.
Liu, P., Ptacek, C. J., & Blowers, D. W. Release of nutrients and trace elements from wood-, agricultural residue-, and manure-based biochars. *Int J Environ Res* 13, 747–750 (2015). <https://doi.org/10.1007/s41742-015-00209-5>
Mullins, C. (2009). *Phosphorus, Agriculture and the Environment*. Virginia Cooperative Extension, 1–18. Retrieved December 21, 2021, from <https://efotg.sc.egov.usda.gov/references/public/va/PhosphorousAgEnv.pdf>
National Oceanic and Atmospheric Administration. (2019, April 2). *What is Eutrophication?*

NOAA's National Ocean Service. Retrieved January 31, 2022, from <https://oceanservice.noaa.gov/facts/eutrophication.html>
Tao, X., Huang, T., & Lv, B. (2020). Synthesis of Fe/MG-biochar nanocomposites for phosphate removal. *Materials*, 13(4), 816. <https://doi.org/10.3390/ma13040816>
Werner, S., Kästel, K., Wichern, M., Buerkert, A., Steiner, C., Marschner, B. Agronomic benefits of biochar as a soil amendment after its use as waste water filtration medium. *Environ Pollut*. 2018 Feb;233:561-568. doi: 10.1016/j.envpol.2017.10.048. Epub 2017 Nov 5. PMID: 29102886.
Yao, Y., Gao, B., Zhang, M., Inyang, M., & Zimmerman, A. R. (2012). Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere*, 89(11), 1467–1471. <https://doi.org/10.1016/j.chemosphere.2012.06.002>
Yi, M., & Chen, Y. (2018). Enhanced phosphate adsorption on Ca-mg-loaded biochar derived from tobacco stems. *Water Science and Technology*, 78(11), 2427–2436. <https://doi.org/10.2166/wst.2019.001>
Books:
Lehmann, J., & Joseph, S. (2009). *Biochar for Environmental Management*. Earthscan.
Images:
Patel, K., & Stevens, J. (2019). *Eerie blooms in Lake Erie*. NASA. Retrieved May 13, 2022, from <https://earthobservatory.nasa.gov/images/145453/eerie-blooms-in-lake-erie>
Back to the future: Terra Preta – Ancient Carbon Farming System for Earth Healing in the 21st Century. The Permaculture Research Institute. (2013, October 14). Retrieved May 7, 2022, from <https://www.permaculturenews.org/2010/05/25/back-to-the-future-terra-pret-a-42x80953-ancient-carbon-farming-system-for-earth-healing-in-the-21st-century/>