Sustainable phosphorus management: Reuse of recovered phosphorous in agriculture and Impact of agricultural management practices on phosphorus speciation

by

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B.S., University of Peradeniya, 2014
M.S., University of Peradeniya, 2017

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Agronomy
College of Agriculture

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2023

Abstract

The vital crop nutrient phosphorous (P) is essential in maintaining food security for a continuously growing world population. However, the mined rock phosphate, the primary P fertilizer source, will eventually become scarce as it is exploited at higher rates. Although applying nutrients to agricultural systems has resulted in a remarkable increase in yield, overloading nutrients to soil leads to environmental concerns, such as eutrophication and harmful algal blooms in surface waters. Therefore, the sustainable management of nutrients is a challenge, and exploring safe and efficient secondary P fertilizer sources is crucial. Wastewater is a renewable resource and recovered nutrient products (RNPs) from wastewater may contain high concentrations of plant-available nutrients such as P and are thus promising alternative fertilizers. The first three studies evaluated the effectiveness of contrasting groups of RNPs (Fe- and Ca-based) recovered from Fort Riley, Kansas municipal wastewater, synthetic, and real swine wastewater using an innovative anaerobic membrane bioreactor (AnMBR) technology. The objectives were to characterize the RNPs and compare the dissolution, transformations, and potential bioavailability of P in RNPs with conventional P fertilizers in selected calcareous, neutral, and acidic soils using short-term laboratory incubation studies. The RNPs were characterized using wet chemical methods, laboratory-based X-ray diffraction, scanning electron microscopy-energy dispersive X-ray, and X-ray absorption near edge structure (XANES) spectroscopy. The soil pH, total P (to assess diffusion), and resin extractable P (to assess potential plant availability) were measured in a spatially resolved manner with XANES spectroscopy in incubation study soil samples. While Fe was used for P recovery in municipal wastewater, the resulting RNP was rich in Fe-P, and as Ca was used for P recovery in synthetic and real swine wastewater, their resulting RNPs were rich in Ca-P. All tested RNPs showed less

performance than the conventional fertilizers used. The Ca-based RNPs acted as a P source, and Fe-based RNP acted as a P sink for tested soils. Therefore, optimizing Ca-based RNP recovery will likely offer applicable secondary P sources for agriculture. The Fe-based RNP may be used as a P sink in specific agricultural systems where excessive P runoff threatens the ecosystem from land-applied P.

Phosphorus loss from non-point agricultural sources is a crucial contributor to decreased surface water quality. Phosphorus can be found in both dissolved and sediment-bound forms in agricultural runoff. The dissolved P is mainly in the form of orthophosphate. Sediment-bound P is sorbed to the soil minerals and organic material in surface runoff. Although not readily available, sediment-bound P can contribute to continued eutrophication upon transformation to bioavailable P. Overall aims of the last study were to characterize and evaluate the effects of a five-year-long fertilizer (placement and source) and cover crop management on P speciation in surface runoff sediments and source soil collected from the Kansas Agricultural Watershed (KAW) field laboratory in Manhattan, Kansas. Runoff samples collected throughout 2020 and the source soil collected in 2019 fall were analyzed using a modified sequential extraction scheme for indirect P speciation. Direct P speciation was done using XANES spectroscopy. The P fractionation results showed that P and cover crop management affected the exchangeable, organic-associated, and iron-bound P fractions in sediments and exchangeable and residual fractions in source soil. The XANES analysis showed a depletion of iron-associated P in soil and sediment from cover crop systems, suggesting that changes in iron-associated P play a vital role in the solubility of P in different management systems. This study contributes to the mechanistic understanding needed in developing P fertilizer and cropping system management options that improve agricultural and environmental sustainability.

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Acknowledgements

I would like to express my sincere gratitude to my major advisor, Dr. Ganga M. Hettiarachchi. I am forever grateful for her guidance, professional mentorship, patience, care, and encouragement over all these years. I'm so blessed to be a member of her lab group, where we have the freedom to think, develop, and build up as better researchers and a friendly working environment.

I would also like to thank my Ph.D. committee members Dr. Dorivar Ruiz Diaz, Dr. Eduardo Santos, Dr. Prathap Parameswaran, and Dr. Stacy Hutchinson for their valuable insights and feedback.

I would also like to thank Dr. Nathan Nelson, all KAW project instigators, the KAW project team, and the Advanced Wastewater Treatment and Resource Recovery lab group, Department of Civil Engineering, KSU, for all their support throughout this journey.

I appreciate all my friends and colleagues, former and current members of the soil and environmental soil chemistry lab, KSU, Dr. Buddhika Galkaduwa, Dr. Jay Weeks, Dr. Zafer Alasmary, Dr. Mohammad Almutari, Dr. Ruwandi Kumarashinghe, Sevendeep Kaur, Manjot Rekhi, Chandima Wekumbura, Eduardo Brito, Nishadi Dodampe Mudiyanselage, Amila Emihami Mudiyanselage and Jack Murphy. Also, all the laboratory assistants in the lab helped me over the years.

I would also like to acknowledge the Soil Test Laboratory and the Department of Agronomy. Also, thank you to Advanced Photon Source, Argonne National Lab, Chicago, IL., for providing the invaluable opportunity to use their synchrotron facilities, especially to the beamline scientists at Sector 9 BM-B, for their help.

I would like to acknowledge the funding support that made my research possible from the USDA National Institute of Food and Agriculture Exploratory Grant, Award Number:2017-09353, Hatch-Multistate project 1024541, KSU Global Food Systems seed grants: NECESEEDPP 0190 (2019-2020) and NECESEEDPP 0190 (2021-2022), KAW Project: Funded by FFAR Grant # CA19-SS-0000000022, KDA and Kansas Soybean Commission; NRCS KAW water quality Grant.

I would also thank the Department of Soil science, Faculty of Agriculture, University of Peradeniya, where my roots are.

Finally, I am very grateful to my loving mother, father, and brother for their continuous love, support, and encouragement. I would like to thank my mother and father-in-law for their support. Also, thank all my friends and family here in Manhattan and Sri Lanka for all their support. I also thank my husband, Amila, for always being by my side throughout this journey. Finally, I would like to thank my son Senith for cheering me up every day.

Dedication

To my loving son, husband, parents, and brother!

Your unconditional love, encouragement, and support made this journey possible!

Chapter 1 - Introduction

Agronomy is a complex scientific discipline that has numerous challenges. However, by implementing best practices, we can ensure that crops receive adequate nutrition to sustain our growing population. Phosphorus (P) is a critical macronutrient in maximizing crop production and improving food and feed quality. It is a component in all cell membranes, RNA, and DNA and aids in transferring energy within the cells. It only comes from the soil for such a diverse group of uses of P. The average total P concentration in soils is 600 mg kg^{-1} (Lindsay, 1979), where the median is 800 mg kg^{-1} and generally ranges from 35 mg kg^{-1} to 5300 mg kg^{-1} (Essington, 2015). Regardless of the soil total P concentrations, soil P availability is limited. Worldwide, billions of hectares of farmland possess yield-limiting concentrations of labile P (Dhillon et al., 2017). To remedy this situation, growers annually apply millions of tons of fertilizer to various agricultural systems. The Primary P fertilizer source used in agriculture is derived from mined rock phosphate. The global demand for phosphorus fertilizer is projected to increase by 50–100% by 2050, enabling sustained food production for a growing world population (Godfray et al., 2010). Global P scarcity is expected to be one of the most significant barriers to food production in the 21st century, given its dependence on mining non-renewable phosphate rock (Cordell et al., 2011). Therefore, complete reliance on P fertilizer manufactured from mined phosphate rock may not be a good strategy for sustained crop yields, stimulating the need to find alternative P sources and recycling of P from municipal, agricultural, and other biodegradable waste sources as green renewable fertilizers with high P use efficiency (Syers et al., 2008; Ma et al., 2011; Schroder et al., 2011; Huang et al., 2012; Zhang et al., 2013).

Effective resource recovery, mainly harvesting nutrients and energy from wastewater, could revolutionize the interrelationships between food, energy, and water systems. Wastewater

is a renewable resource containing nutrients such as nitrogen (N) and P. Currently, recovered energy and nutrient value are only about 25–30% of the total available waste biomass, and between 30–80% of N and 15–18% of P from a variety of livestock wastes are lost before to any form of recovery (Mayer et al., 2016). The Water Environment Federation refers to "Wastewater Treatment Facilities" as "Water and Resource Reclamation Facilities." This change represents a paradigm shift within the water sector. It shows a significant ongoing effort to develop existing technologies further or develop new technologies to recover nutrients for different agricultural uses. Anaerobic membrane bioreactors are an emerging environmental biotechnology platform to simultaneously recover water, energy, and nutrients from various concentrated wastewater (Liao et al., 2006; Lin et al., 2013). This technology combines the techniques of anaerobic biological treatment and membrane filtration. A pilot-scale gas sparged AnMBR successfully operating at Kansas State University and treats wastewater with seasonally varying temperatures that included dissolved methane recovery using a membrane contactor, sulfide and P recovery using coagulation, flocculation, and sedimentation and ammonia capture (Lim et al., 2019; Kannan & Parameswaran, 2021; Kannan et al., 2023).

The nutrient contents in the Recovered Nutrient Products (RNPs) reclaimed from wastewater may vary by composition, characteristics, and treatment technologies. In municipal wastewater in anaerobic systems, mineral vivianite is known to precipitate, emerging as an alternative for P recovery (Rothe et al., 2016; Wilfert et al., 2018). Most studies on P removal from animal wastewater, including swine and dairy wastewater, have focused on struvite recovery (Huang et al., 2016; Rabinovich et al., 2018; Le et al., 2021). There are limited studies on the exclusive recovery of calcium phosphate from swine wastewater (Szogi et al., 2018).

However, limited data are available on the potential use of RNPs as a secondary P source in different soils.

On the other hand, agricultural production has been identified as a significant source of sediment, N, and P pollution, leading to surface water quality issues (Sharpley & Tunney, 2000). Phosphorus is the "limiting nutrient" in fresh waters (Correll, 1999). Therefore, sustainable management of nutrients in agricultural systems has become a grand challenge for the 21st century (Zhang et al., 2020). It is estimated that up to 70% of all P that reaches surface waters is linked to a nonpoint agricultural source (Havlin et al., 2005). In many soils, including those across the United States, a significant portion of the applied P is rapidly converted to forms that plants cannot readily use, resulting in wastage of grower capital and creating environmental hazards. The increase in P pollution to surface water is especially detrimental, although not exclusive, to freshwater bodies (Moody, 2011). Soils containing elevated levels of plant-unavailable forms of P erode into lakes and streams, nourishing cyanobacteria that produce the toxic blooms that endanger biodiversity, recreational opportunities, and drinking water quality (Jarvie et al., 2017). As per the reports of the US EPA 2009 and 2013, it has been found that there are high levels of N and P eutrophication in more than a quarter of streams and one-fifth of lakes in the United States. In the past few decades, there has been an increase in marine eutrophication globally as well (Ngatia et al., 2019). The development of the world's second-largest coastal hypoxic zone during summertime in the northern Gulf of Mexico is mainly caused by excessive N and P loadings, which primarily come from anthropogenic sources (Sylvan et al., 2006; Dale et al., 2008; Tan et al., 2021). Eutrophication and associated HABs are conservatively estimated to cost the United States economy 2.4-4.6 billion dollars a year (Dodds et al., 2009). In addition to severe economic impact, harmful algal blooms increase the risk of

adverse health impacts on humans and animals (Hudnell, 2010). Many studies have revealed that there is a high willingness to pay for benefits associated with water quality, such as recreational activities, including swimming, fishing, and boating at local and regional scales (Johnston et al., 2005; Zhang & Sohngen, 2018; Wolf et al., 2019; Gourevitch et al., 2021).

Both erosion and surface runoff are important processes for understanding mechanisms leading to P loss (Pierzynski et al., 2005). Sharpley et al., 1994 documented that the surface runoff volume, sediment concentration of surface runoff, and form and concentration of P in the soil directly influence the amount of P lost in surface runoff. In agricultural runoff, P can be found in dissolved or sediment-bound forms. The dissolved P is mainly in orthophosphate form, commonly known as molybdate reactive P or dissolved reactive P. Sediment P is sorbed to the soil minerals and organic material in surface runoff. Although not readily available, sediment P helps to maintain control of dissolved P. Therefore, it may contribute to continued eutrophication.

Therefore, to address environmental concerns such as erosion, nutrient loss, and water pollution, the United States Department of Agriculture, Natural Resources Conservation Service (USDA NRCS) promotes conservation practices such as changes in tillage practices and planting cover crops designed to reduce erosion and pollution while improving soil health (NRCS, 2015). Many farmers have adopted conservation tillage practices instead of conventional tillage systems to combat erosion losses. Conservation tillage is a sequence of tillage practices that lead to a reduction in soil or water loss compared to conventional tillage while leaving at least 30% of the soil surface covered by residuals, including practices such as strip-tillage, ridge-tillage, mulch-tillage, and no-tillage (Brady & Wiel, 2002). Planting cover crops during regular fallow periods is a commonly cited management practice to help reduce nutrient loss through erosion (De Baets

et al., 2011). A cover crop is any living ground cover sown before, during, or after a main crop and then terminated before planting the next crop (Hartwig & Ammon, 2002). The benefits of cover crops could include more significant understanding of how management practices (tillage, cover crop, P fertilizer) contribute to source soil and sediment P speciation is essential to implementing necessary management practices to mitigate P losses. However, several knowledge gaps exist for no-till, cover crops, and P fertilizer management in agricultural systems.

In this dissertation, four studies explored the RNPs recovered from different wastewaters, their potential use in agriculture as a secondary P source, and how P fertilizer and cover crop management contribute to soil and sediment P speciation in no-till corn and soybean rotation.

Research objectives

1. The objectives of the first study were to characterize and compare the Fe-based RNPs recovered from municipal wastewater using an innovative AnMBR technology, and to investigate the dissolution, transformations, and potential bioavailability of P in the Fe-based RNP with conventional P fertilizers in a selected calcareous soil using short-term laboratory incubation studies combined with wet chemical and synchrotron-based x-ray techniques.

2. The objectives of the second study were to characterize and compare the Ca-based RNPs recovered from synthetic swine wastewater using AnMBR technology, and to investigate the dissolution, transformations, and potential bioavailability of P in RNP with conventional P fertilizers in selected calcareous, neutral, and acidic soils using short-term laboratory incubation studies combined with wet chemical and synchrotron-based x-ray techniques.

3. The objectives of the third study were to characterize and compare the Ca-based RNPs recovered from swine wastewater using an innovative AnMBR technology, and to investigate the dissolution, transformations, and potential bioavailability of P in RNP with

conventional P fertilizers in a selected neutral soil using short-term laboratory incubation studies combined with wet chemical and synchrotron-based x-ray techniques.

4. The objectives of the fourth study were to characterize and evaluate the effects of a five-year-long fertilizer (placement and source) and cover crop management on P speciation in surface runoff sediments from natural precipitation events and source soil collected from Kansas Agricultural Watershed (KAW) field laboratory Manhattan, Kansas under no-till corn (*Zea mays* L.)-soybean (*Glycine max* L.) rotation.

References

Brady, N. C., and R. R. Well. 2002. The nature and properties of soil. Pearson Education, Inc., NJ

Cordell, D., A. Rosemarin, J. Schröder, and A. Smit. 2011. Towards Global Phosphorus Security: A Systems Framework for Phosphorus Recovery and Reuse Options. Chemosphere. 84, 6: 747-758.

Correll, D. L., 1999. Phosphorus: a rate limiting nutrient in surface waters. Poult. Sci. 78: 674-682. https://doi.org/10.1093/ps/78.5.674.

Dale, V., T. Bianchi, A. Blumberg, W. Boynton, D. J Conley, W. Crumpton, M. David, D. Gilbert, R.W. Howarth, C. Kling, R. R. Lowrance, K Mankin, J. L. Meyer, J. Opaluch, H. Paerl, K. Reckhow, J. Sanders, A. N. Sharpley, T. W. Simpson, C. Snyder, D. Wright, H. Stallworth, T. Armitage, and D. Wangsness. 2008. Hypoxia in the Northern Gulf of Mexico: An update by the EPA Science Advisory Board. Environmental Protection Agency. 333. (Technical Report)

De Baets, S., J. Poesen, J. Meersmans, and L. Serlet, L. 2011. Cover crops and their erosion reducing effects during concentrated flow erosion. Catena. 85:237–244.

Dhillon, J., G. Torres, E. Driver, B. Figueiredo, and W.R. Raun. 2017. World phosphorus use efficiency in cereal crops. Agron. J. 109:1670-1677.

Dodds, W. K., J. L. Eitzmann, T. J. Pilger, K. L. Pitts, A. J. Riley, J. T. Schloesser and D. J. Thornburgh. 2009. Eutrophication of U.S. freshwaters: Analysis of potential economic damages. Environ. Sci. Technol. 43:12-19.

Essington, M. E., 2015. Soil and Water Chemistry: An Integrative Approach. CRC press.

Godfray, H. C. J., J. R. Beddington, I. C. Crute, L. Haddad, D. Lawrence, J. F. Muir, J. Pretty, S. Robinson, S. M. Thomas, and C. Toulmin. 2010. Food security: the challenge of feeding 9 billion people. Science. 327(5967): 812-818. http://dx.doi.org/10.1126/science.1185383

Gourevitch, J. D., C. Koliba, D. M. Rizzo, A. Zia, and T. H. Ricketts. 2021. Quantifying the social benefits and costs of reducing phosphorus pollution under climate change. J. Environ. Manage. 293: 112838. https://doi.org/10.1016/j.jenvman.2021.112838

Hartwig, N. and H. Ammon. 2002. 50th anniversary - invited article - cover crops and living mulches. Weed Sci. 50: 688-699.

Havlin, J. L., J. D. Beaton, S. L. Tisdale and W. L. Nelson. 2005. Soil fertility and fertilizers: An introduction to nutrient management. Pearson Education, Upper Saddle River, New Jersey.

Huang, H., P. Zhang, Z. Zhang, J. Liu, J. Xiao, and F. Gao. 2016. Simultaneous removal of ammonia nitrogen and recovery of phosphate from swine wastewater by struvite electrochemical precipitation and recycling technology. J. Clean. Prod. 127. 302–310.

Huang, X. L., Y. Chen, and M. Shenker. 2012. Dynamics of phosphorus phytoavailability in soil amended with stabilized sewage sludge materials. Geoderma. 170: 144–153.

Hudnell, H. K. 2010. The state of US freshwater harmful algal blooms assessments, policy, and legislation. Toxicon. 55:1024-1034.

Jarvie, H. P., L. T. Johnson, A. N. Sharpley, D. R. Smith, D. B. Baker, T. W. Bruulsema, and R. Confesor. 2017. Increased soluble phosphorus loads to Lake Erie: Unintended consequences of conservation practices?. J. Environ. Qual. 46:123-132.

Johnston, R. J., E. Y. Besedin, R. Iovanna, C. J. Miller, R. F. Wardwell, and M. H. Ranson. 2005. Systematic variation in willingness to pay for aquatic resource improvements and implications for benefit transfer: a meta-analysis. Can. J. Agric. Econ. 53: 221-248.

Kannan, A. D. J. Dillavou, K. H. H. Gamage, E. Randig, G. M. Hettiarachchi, and P. Parameswaran. 2023. Recovery of high-quality calcium phosphate fertilizer products from anaerobic membrane bioreactor treated swine wastewater. J. Chem. Eng. 453:1. 139539. https://doi.org/10.1016/j.cej.2022.139539

Kannan, A. D., and P. Parameswaran. 2021. Ammonia adsorption and recovery from swine wastewater permeate using naturally occurring clinoptilolite. J. Water Process. Eng. 43: 102234.

Le, V. G., D. V. Vo, N. H. Nguyen, Y. J. Shih, C. T. Vu, C. H. Liao, and Y. H. Huang. 2021. Struvite recovery from swine wastewater using fluidized-bed homogeneous granulation process. J. Environ. Chem. Eng. 9 (3): 105019.

Liao, B.Q., J. T. Kraemer and D. M. Bagley. 2006. Anaerobic Membrane Bioreactors: Applications and Research Directions. Crit Rev Environ Sci Technol. 36: 489–530.

Lim, K., P. J. Evans, and P. Parameswaran. 2019. Long-Term Performance of a Pilot-Scale Gas-Sparged Anaerobic Membrane Bioreactor under Ambient Temperatures for Holistic Wastewater Treatment. Environ. Sci. Technol. 53(13): 7347–7354. https://doi.org/10.1021/acs.est.8b06198

Lin, H., W. Peng, M. Zhang, J. Chen, H. Hong and Y. Zhang. 2013. A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives. Desalination. 314: 169–188.

Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Ma, W. Q., L. Ma, J. H. Li, F. H. Wang, I. Sisak, and F. S. Zhang. 2011. Phosphorus flows and use efficiencies and consumption of wheat, rice, and maize in China. Chemosphere. 84: 814–821.

Mayer, B. K., L. A. Baker, T. H. Boyer, P. Drechsel, M. Gifford, M. A. Hanjra, P. Parameswaran, J. Stoltzfus, P. Westerhoff, and B. E. Rittmann. 2016. Total Value of Phosphorus Recovery. Environ. Sci. Technol. 50(13): 6606–6620. https://doi.org/10.1021/acs.est.6b01239

Moody, P. W. 2011. Environmental risk indicators for soil phosphorus status. Soil Res. 49: 247-252.

Ngatia, L., M. Grace III, J., Moriasi, D., & Taylor, R. (2019). Nitrogen and Phosphorus Eutrophication in Marine Ecosystems. IntechOpen. doi: 10.5772/intechopen.81869

NRCS. 2015. Soil health literature summary – Effects of conservation practices on soil properties in areas of crop land. Natural Resources Conservation Service, National Soil Survey Center. United States Department of Agriculture.

Pierzynski, G. M., R. W. McDowell, and J. T. Sims. 2005. Chemistry, cycling, and potential movement of inorganic phosphorus in soils. In J. Sims and A. Sharpley, (eds.) Phosphorus: Agriculture and the environment. ASA, CSSA, SSSA, Madison, WI.

Rabinovich, A., A.A. Rouff, B. Lew, and M.V. Ramlogan. 2018. Aerated fluidized bed treatment for phosphate recovery from dairy and swine wastewater. ACS Sustain. Chem. Eng. 6 (1): 652–659.

Rothe, M., A. Kleeberg, and M. Hupfer. 2016. The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments. Earth Sci. Rev. 158: 51–64. https://doi.org/10.1016/j.earscirev.2016.04.008

Schroder, J. J., A. L.Smit, D. Cordell, and A. Rosemarin. 2011. Improved phosphorus use efficiency in agriculture: A key requirement for its sustainable use. Chemosphere. 84: 822–831.

Sharpley, A., and H. Tunney. 2000. Phosphorus research strategies to meet agricultural and environmental challenges of the 21st Century. J. Environ. Qual. 29: 176-181.

Sharpley, A. N., S. C. Chapra, C. R. Wedepohl, J. T. Sims, T. C. Daniel and K. R. Reddy. 1994. Managing agricultural phosphorus for protection of surface waters: Issues and options. J. Environ. Qual. 23:437-451.

Syers, J. K., A. E. Johnston, and D. Curtin. 2008. Efficiency of Soil and Fertilizer Phosphorus Use. FAO Fertilizer and Plant Nutrition Bulletin. FAO, Rome.

Sylvan, J. B., Q. Dortch, D. M. Nelson, A. F. Maier-Brown, W. Morrison, and J. W. Ammerman. 2006. Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation Environ. Sci. Technol. 40: 7548–53.

Szogi, A. A., M.B. Vanotti, P.D. Shumaker. 2018. Economic recovery of calcium phosphates from swine lagoon sludge using Quick Wash process and geotextile filtration. Front. Sustain. Food Syst. 2: 37.

Tan, Z., L. R. Leung, H.-Yi. Li, T. Tesfa, Q. Zhu, X. Yang, Y. Liu, and M. Huang. 2021. Increased extreme rains intensify erosional nitrogen and phosphorus fluxes to the northern Gulf of Mexico in recent decades. Environ. Res. Lett. 16(5). https://iopscience.iop.org/article/10.1088/1748-9326/abf006/meta

US EPA. 2009. National lakes assessment: a collaborative survey of the Nation's lakes EPA 841-R-09-001 (Washington, DC: U.S. Environmental Protection Agency).

US EPA. 2013. National rivers and streams assessment (NRSA) 2008−2009 draft report EPA/841/D-13/001 (Washington, DC: U.S. Environmental Protection Agency).

Wilfert, P., A. I. Dugulan, K. Goubitz, L. Korving, G.J. Witkamp, and M.C.M. Van Loosdrecht. 2018. Vivianite as the main phosphate mineral in digested sewage sludge and its role for phosphate recovery. Water Res. 144: 312–321. https://doi.org/10.1016/j.watres.2018.07.020

Wolf, D., W. Chen, S. Gopalakrishnan, T. Haab, and H.A. Klaiber. 2019. The impacts of harmful algal blooms and E. coli on recreational behavior in lake erie. Land Econ. 95: 455-472.

Zhang, W., and B. Sohngen. 2018. Do US anglers care about harmful algal blooms? A discrete choice experiment of Lake Erie recreational anglers. Am. J. Agric. Econ. 100: 868-888.

Zhang, X. D., H. Spanjers, and J.B. van Lier. 2013. Potentials and limitations of biomethane and phosphorus recovery from sludges of brackish/marine aquaculture recirculation systems: A review. J Environ Manage. 131: 44–54.

Zhang, X., E. A. Davidson, T. Zou, L. Lassaletta, Z. Quan, T. Li, and W. Zhang. 2020. Quantifying Nutrient Budgets for Sustainable Nutrient Management. lobal Biogeochem. Cycles. 34(3).

Chapter 2 - Review of Literature

2.1. Role of phosphorus

Phosphorus (P) is an essential element for all life forms. It is used not only in the fertilizer industry but extensively in a variety of applications such as soft drinks, pharmaceuticals, biomaterials, and flame retardants (Qiu et al., 2019; Duhamel et al., 2021; Jupp et al., 2021). Plant P exists as the free inorganic orthophosphate form (P_i) or as an organic phosphate ester (Veneklaas et al., 2012). The P_i concentration of tissues generally reflects the P_i supply, which is true in crop plants (White & Hammond, 2008). Phosphorus is a major structural component of DNA and RNA. The nucleic acid pool is typically the largest organic P pool in a plant, generally containing 40–60% of the P found in the combined organic P pool (Veneklaas et al., 2012). The P is an essential element in converting the sun's energy into chemical energy, and it plays a key role in transporting energy to every cell in the plant. There are many uses of P for plants, which include early root growth, flowering, fruiting stimulation, and hastens maturity. It is often a limiting nutrient in crop production. Stunted growth, abnormal dark green color, and purplish leaves in corn also indicate P deficiency.

2.2. Phosphorus cycle in soil

The P cycle within a soil system is a complex process involving various pools, inputs, outputs, inorganic, organic, and microbial processes, and transformations of P (Figure 2.1). Plants, microorganisms, climate, temperature, moisture, and parent material influence it. (Pierzynski et al., 2005). The average total P concentration in soils is 600 mg kg^{-1} (Lindsay, 1979). The median of total soil P concentration is around 800 mg kg^{-1} and it generally ranges from 35 mg kg^{-1} to 5300 mg kg^{-1} (Essington, 2015). Phosphorus exists within various pools of

varying solubility, including very labile forms, which are sorbed or present as discrete solid phases or as part of soil organic matter.

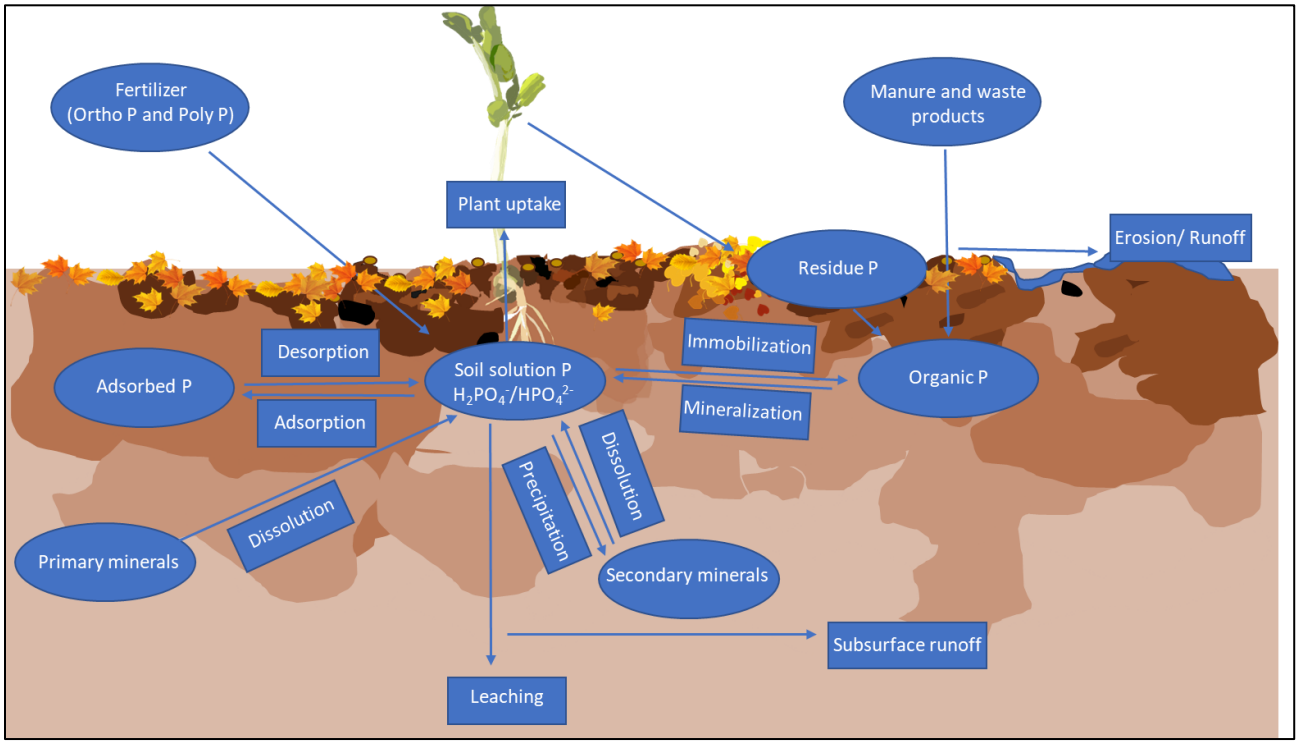


Figure 2.1. Soil phosphorus cycle

The P inputs to the soil system influence or promote P chemical reactions and transformations. Inputs include the addition of fertilizers, either inorganic P fertilizers or organic-based by-products such as composted manure, as well as decomposing plant residue. In addition, above and below-ground decaying plant residue releases P back into the soil in organic forms, eventually released as inorganic P. Over time, plants will take up part of the applied P, and most of it reacts with other soil components to form insoluble P forms (Hansen et al., 2002). In agriculture systems, not all P added is returned to the soil. Phosphorus contained in biomass or grain is removed, resulting in a loss of P from the soil P cycle. Other P outputs include run-off of

sediment-bound P, particulate and soluble organic P, and leaching of P through the soil to groundwater and eventually into open or surface waters (Sharpley et al., 2015). Inputs and outputs of P greatly influence P sorption, precipitation, and immobilization in different pools.

The P in soil solution is in equilibrium with labile P pools. There is a very low concentration of P in soil solution ranging from 0.001 mg/L to 1 mg/L in very infertile soil to heavily fertilized soil (Brady & Well, 2002). Soil solution P has inorganic dissolved forms as primary (PO_4^{3-}) or secondary (HPO_4^{2-} and $H_2PO_4^-$) orthophosphates depending on the soil pH, which is available for plant uptake. In alkaline soils, divalent HPO_4^{2-} ions dominate, and in acidic soils, monovalent $H_2PO_4^-$ ions dominate. Inorganic forms of P in soil account for 50-70% of total P, while organic forms account for 30-50% of total P (Carman et al., 2000). Inorganic P forms in soil include mineral P forms, adsorbed P forms and Occluded P. Within soils, the principal primary P mineral is apatite, $Ca_{10}(PO_4)_6(X)$, where the X represents Cl^-, CO_3^{2-}, F^- or OH^-, with fluorapatite being the most important (Pierzynski et al., 2005). In highly weathered soil, basic cations slowly leached through the profile, decreasing the soil pH and leaving behind the Fe and Al mineral forms where solution P can precipitate with free Al or Fe or become strongly sorbed to Fe and Al oxy-hydroxide and hydrous oxide minerals resulting in very low P plant availability (Sanchez & Uehara, 1980). In calcareous soils, the dissolution of P can be minimal and added P is rapidly precipitated with free Ca (Montalvo et al., 2014).

Secondary P mineral precipitation-dissolution processes occur in temperate soils over time, in conjunction with P and Fe, Al, or Ca. These processes continue the sorption-process component and result in the formation of amorphous or crystalline solid phases. In acid soils, some of the important secondary P solid-phase species with their equilibrium constants include variscite (log K = -2.50) and strengite (log K = -6.85) (Lindsay, 1979). In calcareous soils,

primary calcium P species are dicalcium phosphate dihydrate (log K = 0.63), monocalcium phosphate (log K = -1.15), octa calcium phosphate (log K = 11.76), and hydroxyapatite (log K = 14.46) (Lindsay, 1979).

In tropical or acid soils, P sorption-desorption processes happen on the surfaces of Fe and Al oxy-hydroxide solid phases along the open edges of clay minerals or in calcareous soils on carbonates and Fe or Al oxides. The adsorption reaction displaces OH^- or H_2O, and the reactions may be mono- or bidentate as inner-sphere or outer-sphere complexes (Essington, 2015). This is the most labile or available P pool as orthophosphate is removed from the soil solution, such as in plant uptake, adsorbed or sorbed P is released to re-equilibrate with soil solution P. Inner-sphere complex species (specific adsorption) are the majority of P (Sposito, 1989) formed when the ligand displaces water of hydration from the coordination sphere of the metal ion (Essington, 2015). Other P is outer-sphere complex species (non-specific adsorption) or diffuse ion swarm (Sposito, 1989). An outer-sphere complex is formed when the ligand does not displace surface-bound water but forms a metal-water-ligand-bound complex (Essington, 2015). The more stable form is the inner-sphere complexed P, and those complexes are stronger than the outer-sphere complexed P.

2.3. Speciation of phosphorus

Speciation is identifying the exact chemical form or compound in which an element exists in a sample (IUPAC, 2000). An example of P involves determining whether P appears in the state of Fe-, Al-, or Ca-P or as part of an organic molecule and also the quantitative distribution of the different chemical forms of P within a system. The chemical form (speciation) regulates an element's availability, mobility, transport, and fate. Individual metals have different chemical activity and fate depending upon the oxidation state, which determines their fate and

toxicity in the environment. The speciation helps to develop effective remedial plans and risk management at contaminated sites for lead and arsenic-like elements, whereas, for elements like P, speciation helps to build soil and fertilizer management approaches, ensuring the highest bioavailability to crops while protecting the environment.

There are different methods for the speciation of P in soil. Some indirect methods include solubility equilibria and sequential extraction (fractionation procedures). Although non-definitive, these are used to determine possible solid-phase associations of elements of interest in soil or sediment. Indirect are more easily adopted and accessible. However, they often need to complement the direct speciation results for an accurate interpretation. Some of the direct methods of speciation include X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), Fourier transform infrared resonance (FTIR) spectroscopy, and Nuclear Magnetic resonance (NMR) spectroscopy. However, these techniques are sophisticated and may not be regularly accessible. This literature review only focuses on selected techniques.

2.3.1. Sequential extraction/ chemical fractionation method

The chemical fractionation technique is the most commonly used method for partitioning P into different “operationally defined” fractions of P, such as Fe, Al, and Ca-P in soil and sediments. The most popular fractionation techniques are Chang & Jackson, 1957, Hedley et al., 1982, Tiessen et al., 1984 for soils, and Ruttenberg, 1992 for sediments. This technique uses the ability of different chemical reagents to selectively solubilize the Fe, Al, or Ca phosphate phases in the soil/sediments. Kashem et al., 2004 and Ajiboye, 2007 documented that his technique is beneficial in understanding the controlling phases of soil P dynamics. However, this technique suffers from intrinsic limitations such as artifacts associated with reagent selectivity and the inability to differentiate specific solid-state P forms (e.g., amorphous versus crystalline mineral P

phases) (Li et al., 2015). Toor et al., 2006 also documented that the exact confirmation of extractants solubilized exclusively by the target P fraction needs to be improved. Also, the nature of organic P estimated from fractionation is less well-defined than inorganic fractionation (Tiessen et al., 1994). It is implausible that any extraction procedure can provide an exact separation of different P compounds. In recent years, advanced spectroscopic techniques such as XANES have been increasingly applied to complement these extraction methods for a better interpretation of data (Kizewski et al., 2011; Liu et al., 2013; Li et al., 2015; Beauchemin et al., 2003; Ajiboye et al., 2007).

2.3.2. Scanning electron microscopy-energy dispersive X-ray (SEM- EDX) analysis

A scanning electron microscopy (SEM) is a high-magnification microscope often combined with energy-dispersive X-ray spectroscopy. A scanning electron microscope is used to study topographic, morphological, compositional, and crystallographic information of different unknown materials (White, 2008). A primary electron beam is generated from an electron source in the scanning electron microscope. The primary electron beam is accelerated and demagnified into a smaller beam. It is then deflected in a raster fashion over the area to be imaged. The electron beam and the sample generate signals, including secondary and backscattered electrons, producing secondary and backscattered images (Susan, 2011). Secondary electron images are helpful for morphological and topographical information of samples. The backscattered electron images essentially map out the density of the sample surface. The backscattered mode helps to differentiate elemental information from low and high atomic weight areas, as low-atomic weight areas of the sample emit a low number of backscattered electrons as a high atomic area of a sample (Susan, 2011).

Usually, SEM units are coupled with an energy-dispersive X-ray spectrometer (EDS) detector or a wavelength-dispersive X-ray spectrometer (WDS) detector, and they facilitate the determination of the chemical composition of micro volumes of samples (surface sensitive as the penetration depth is limited). Therefore, that system can gather indirect information about different solid phases present in soil samples.

Scanning electron microscopy technique is used to identify morphological studies of soil minerals (White, 2008). This technique is also used to identify the surface characteristics of fertilizer granules (original and incubated) in soils (Hettiarachchi et al., 2008; Pierzynski & Hettiarachchi, 2018). Also, the SEM-EDX analysis has been used to identify the crystal structure of waste-derived products (Massey et al., 2010). Massey et al., 2010 further used SEM–EDX analysis to differentiate the chemical and physical differences in the recovered materials obtained from dairy and food processing wastewater.

2.3.3. X-ray diffraction (XRD) analysis

The X-ray diffraction technique provides information about the atomic structure of crystalline substances. Its detection limit is about 2 wt.% of the sample (Klug & Alexander. 1974; Ali et al., 2022). The XRD is widely used to identify minerals in rocks and soils (Harris & White, 2008). Most of the P minerals occur in clay-sized fractions. It is required to saturate clay minerals with different cations to differentiate some clay minerals and remove iron oxides and organic materials to get better particle separation (Moore & Reynolds, 1997).

The principle of Bragg's law is followed in the XRD. Identifying minerals through X-ray diffraction involves converting diffraction peaks to d-spacings and comparing them with standard reference patterns (Moore & Reynolds, 1997).

Pierzynski et al., 1990 used the XRD technique in conjugation with other optical electron microscope techniques to isolate and characterize phosphate minerals in clay-sized fractions of excessively fertilized soils. Gungor et al., 2007 used XRD to identify minerals present in dairy manure; however, extensive use of XRD for determining fertilizer reaction products in the soil is limited due to the lower concentration of those minerals in the soil and their poor crystallinity. The XRD technique is also used to identify wastewater-recovered products (Massey et al., 2010; Stratful et al., 2001). Heronemus et al., 2021 also observed different XRD patterns for the same RNP but from a different batch where one had prominent calcite ($CaCO_3$) peaks and lower peak intensities for iron phosphates and aluminum oxides and other no identifiable peaks.

However, using laboratory based XRD for identifying reaction products in soil is limited due to the relatively lower concentration of those minerals to be detected. For better interpretation of results, XRD needs to be used complementarily with other direct methods of P speciation. In addition, some of these weaknesses (i.e., lack of sensitivity) can be overcome by micro-focused synchrotron based XRD (Sharma & Hesterberg, 2020).

2.3.4. X- ray absorption near edge structure spectroscopy (XANES) analysis

The XANES is an advanced technique used for direct, in situ speciation of solid phases (i.e., fertilizer reaction products) regardless of their crystallinity. X-ray absorption near edge structure consists of a pre-edge region (~ 20 eV before the edge) and a post-edge region (~ 100 eV after the edge) (Kelly et al., 2008). The XANES is an element-specific and nondestructive technique (Beauchemin et al., 2003). It provides information on the local molecular bonding environment of the element (Fendorf & Sparks, 1996).

The XANES technique is mainly used to identify the speciation of organic and inorganic P in soil, sediments, and agricultural byproducts (Lombi et al., 2006; Kruse & Leinweber, 2008;

Pierzynski & Hettiarachchi, 2018; Weeks & Hettiarachchi, 2020; Heronemus et al., 2021). Hesterberg et al., 1999 used XANES spectroscopy to distinguish different P solid phases and identified the presence of calcium phosphates in soils with a pH of 7.6. Lombi et al., 2006 and Weeks & Hettiarachchi, 2020 used XANES to identify the reaction products of granular and fluid P fertilizers in calcareous soil, whereas Pierzynski & Hettiarachchi, 2018 used XANES to identify fertilizer products in acid soil. Kruse & Leinweber, 2008 used XANES to differentiate P fractions in fen peat due to peat degradation and sequential extraction. This technology is also used in P speciation in poultry litter (Peak et al., 2002; Toor et al., 2005) and in manure and manure-amended soil (Sato et al., 2005; Gungor et al., 2007). Sato et al., 2005 studied Ca-P formed in soils amended with poultry manure. Ajiboye et al., 2008 used XANES to identify P species in two calcareous soils amended with either MAP or various organic amendments. Massey et al., 2018 and Massey, 2019 used XANES in P recovery studies to characterize recovered products.

The quality of XANES data plays a critical role in obtaining accurate speciation results of soil samples, particularly for certain species with similar XANES spectra. The overall quality of XANES spectra is influenced by several factors, including the uncertainty in selecting standards to fit, the lack of distinguishing spectral features for different P species, and the quality of the spectral data (Kizewski et al., 2011). The XANES technique should be complemented with other techniques for better interpretation of results. Combining different techniques should enhance species identification with less uncertainty (Hettiarachchi et al., 2008; Lombi et al., 2011; Milani et al., 2015).

2.4. Phosphorus fertilizers

Many of the P fertilizers used today were developed in the mid-1900s. Gilbert and Lawes were the ones who came up with single superphosphate in the 1840s, which paved the way for other products like triple superphosphate (Encyclopedia Britannica, 2018). The main advantages of these fertilizers were that they were highly concentrated, soluble, and relatively affordable to apply to soil. However, these properties do not necessarily translate into efficient nutrient use, as a significant percentage of the fertilizer can be lost to the surrounding environment rather than being taken up by the intended crop. The amount of soil solution P that is available shortly after fertilizer application does not always match up with plant uptake, which means that the degree to which the nutrient is used depends on a variety of factors, including fertilizer characteristics, soil properties, climate, and the specific cropping system being used (Syers et al., 2008; Vandamme et al., 2013).

Over the past few decades, researchers and engineers have been striving to create innovative solutions that decrease soil fixation reactions, leading to higher crop P supply and better yields. However, what may work effectively in one situation may be less effective in another. One example is the choice between liquid or granular P. Liquid P solutions tend to decrease fixation significantly in calcareous soils and improve efficiency (Weeks & Hettiarachchi, 2020). Nevertheless, the opposite outcome is often seen in Ultisols, Oxisols, and Andisols, which are rich in Fe and Al (Lombi et al., 2004; Hettiarachchi et al., 2006; Pierzynski & Hettiarachchi, 2018).

As we continue to explore ways to increase crop yields and improve soil health, it is essential to note that there is no one-size-fits-all solution. As sensing and testing technology improves, we can imagine using this knowledge to optimize practices for site-specific nuance

impacting P fate and transport. However, the solutions must be practical and financially feasible for average farmers, which is crucial for the real-world impact of any researcher's work.

2.4.1. Inorganic phosphorus fertilizers

The primary source of inorganic P fertilizers is raw rock phosphate deposits. Such mineral phosphate rock reserves are predominantly located in just a handful of countries, including the United States, China, and Russia, with the largest deposit to date in Morocco, increasing supply chain dependency and impacting global food security (Cordell et al., 2014; Blackwell et al., 2019).

The process of producing P fertilizer involves the use of phosphate rock and sulfuric acid. The phosphate rock is transformed through acidulation into phosphoric acid, which is then used as the foundation for various phosphate fertilizers where gypsum is also produced as a by-product (Havlin, 2005; Leikam & Achorn, 2005). Several additional clarification and purification steps are used in processing to make this product more valuable and applicable to the fertilizer industry. A few commonly used inorganic P fertilizers are ordinary or single superphosphate (SSP) (0-20-0), triple super phosphate (TSP) (0-46-0), diammonium phosphate (DAP) (18-46-0), monoammonium phosphate (MAP) (11-52-0), and ammonium polyphosphate (APP) (10-34-0) or (11-37-0) (IPNI, 2010).

The original inorganic fertilizer was SSP produced by taking finely ground phosphate rock and acidulating it with sulfuric acid. The P compound in SSP is $Ca(H_2PO_4)_2$ (monocalcium phosphate, MCP) and also contains gypsum. This P fertilizer contains around 20% P_2O_5 (8.9% P) and a small percentage of sulfur. Though the transportation costs have caused a decline in the use of SSP, it is still being produced and used in various regions across the globe (Leikam & Achorn, 2005).

Triple super phosphate can contain up to 46% P_2O_5 (20.1% P), depending on where the phosphate rock was mined, and the quality of sulfuric acid used during production. It's interesting to note that TSP and SSP share a similar P compound, $Ca(H_2PO_4)_2$, MCP, but TSP does not contain gypsum.

The ammonium phosphate fertilizers are easy to produce and have a high P_2O_5 content (Leikam & Achorn, 2005). Granular MAP ($NH_4H_2PO_4$), DAP ($(NH_4)_2H_2PO_4$) fertilizer or fluid APP ($(NH_4)_3HP_2O_7$) are the most common ones. Ammonium polyphosphate is one of the most popular forms of liquid P fertilizer today. They contain approximately one-quarter to one-half orthophosphate (OP) and the remainder polyphosphates (PP) (e.g., pyrophosphate, triphosphate) (IPNI, 2010). The condensed P forms typically oxidize to OP by enzymes released from soil microorganisms and plant roots. How quickly the conversion proceeds depends on environmental conditions such as temperature, P concentration, and pH (McBeath et al., 2006; McBeath et al., 2009). One concern is that early-season growth may be compromised when the hydrolysis of PP is slow (McBeath et al., 2006).

2.4.2. Recovered (reclaimed) phosphorus fertilizers

Managing human and animal waste on farms and in populous areas is a worldwide challenge. Therefore, there is an increased focus on wastewater as part of the circular economy (Robles et al., 2020; Roychand et al., 2020). Wastewater contains nutrients such as P and N that can be reclaimed for fertilizer production, energy potential that can be harnessed from organic matter, and water that can be reused (Robles et al., 2020). Many wastewater treatment plants brand themselves as Water Resource Recovery Facilities (WRRFs) to align with this theme.

Wastewater treatment has typically utilized physical and biological methods to eliminate solids and organic materials from the waste to prevent pollution and oxygen depletion. However,

swine waste from small and large Confined Animal Feeding Operations (CAFOs) is usually not treated and stored in an anaerobic lagoon on site, resulting in greenhouse gas emissions and stabilized sediments (Nelson et al., 2003). The anaerobic digestion of this waste is not commonly practiced (Meinen et al., 2014).

The biological nutrient removal (BNR) systems effectively remove N and P from municipal wastewater, with total N and P in discharge produced below 5 mg/L as N and 0.5 mg/L as P (Bashar et al., 2018). In BNR systems, N is transformed into nitrogen gas, and P remains trapped in the settled BNR sludge (Tchobanoglous et al., 2014). Therefore, many options are available for a more effective recovery of P from municipal or agricultural wastewater, apart from removal. Several other widely explored technologies include chemical coagulation and flocculation processes, bio electrochemical systems for further polishing, and membrane-based and photosynthetic-based processes (Robles et al., 2020).

2.4.2.1. Technologies of phosphorus recovery from wastewater

A simultaneous recovery of P and N as phosphate and ammonia is achieved by precipitation of struvite ($MgNH_4PO_4$ or KNH_4PO_4) in the form of a slow-release fertilizer (Sengupta et al., 2015). In the production process of struvite, pH and temperature are carefully controlled to enable crystallization, and chemicals such as magnesium chloride, oxide, or hydroxide are added to complete the precipitation reaction (Pastor et al., 2010; Tchobanoglous et al., 2014). Several companies such as Ostara, CalPerx, Pearl, AirPrex, PHOSPHAQ, Phosnix, and Crystalactor are working with municipal treatment plants to implement various patented processes for struvite precipitation and crystallization and sell the products (Tchobanoglous et al., 2014). These companies market themselves as removing P to meet discharge regulations and helping with research and technology development (Otoo et al., 2015; Mayer et al., 2016).

However, struvite has relatively low P recovery efficiency (10-50% P sequestration efficiency), and this can be achieved only in municipal wastewater treatment plants with enhanced biological P removal (EBPR) (Egle et al., 2015).

Sengupta et al., 2015 also documented that chemical P removal using calcium, aluminum, and iron coagulants is also effective in P recovery. Anaerobic membrane bioreactors (AnMBRs) are a treatment technology that combines anaerobic biological treatment with membrane filtration and gain the benefits of both for a unique combination of biological and physical treatment (Lin et al., 2013; Evans et al., 2018; Lim et al., 2019). It possesses several potential advantages over aerobic treatment processes regarding energy balance, nutrient recovery opportunities, and minimizing sludge production. In addition to reducing energy consumption by avoiding the need for aeration, anaerobic treatment can produce methane-rich biogas that can be combusted for energy recovery, which can push the system to energy neutrality or even energy-positive operation (Smith et al., 2013; Batstone & Virdis, 2014; Hagos et al., 2017). The AnMBRs can achieve high-rate treatment of chemical oxygen demand (COD) as well as 5-day biochemical oxygen demand (BOD_5) (Lin et al., 2013; Smith et al., 2013). These characteristics have led to their successful application in various settings, from industrial treatment to domestic wastewater treatment (Liao et al., 2006; McCarty et al., 2011). There are limited studies on the treatment of swine manure and swine wastewater by AnMBRs, though it is a significant candidate for AnMBR treatment and resource recovery due to its high organic strength (Bu et al., 2017; Cheng et al., 2021). Swine wastewater has much higher organic and nutrient concentrations than municipal wastewater, where the COD in swine wastewater can be as high as 10,000 mg/L, and the P and N concentrations can reach up to 250 mg/L P and 1200 mg/L N, respectively (Cheng et al., 2020). Therefore, P and N concentrations in swine wastewater could

be about 5 - 10 times higher than in municipal wastewater (Henze et al., 2008). Additionally, AnMBRs present another challenge for providing high-quality effluent by reducing the sulfate from the influent to hydrogen sulfide due to the presence of sulfate-reducing bacteria (SRBs) (Kannan et al., 2020).

There is a potential to recover iron phosphate and calcium phosphate using chemical precipitation processes through the AnMBR system. However, detailed agronomic studies and techno-economic analyses on iron and calcium phosphate products are limited (Cornel & Schaum, 2009; Mayer et al., 2016; Robles et al., 2020). Harclerode et al., 2020 conducted a life cycle assessment to compare multiple AnMBR-based domestic wastewater treatment trains to conventional activated sludge treatment. That study determined two process subcomponents (sulfide and P removal and sludge management) that drove chemical use and residual generation and, in turn, the environmental and cost impacts. In that, sulfide and P removal with coagulation using ferric chloride and aluminum chlorohydrate produced approximately twice the total residuals (1.45–1.48 kg/m^3 AnMBR treatment) compared to conventional treatment (0.65 kg/m^3).

2.4.2.1.1. Iron phosphate recovery

A common practice for wastewater treatment plants is iron addition via ferric chloride to control odor from hydrogen sulfide formation to form iron sulfide (FeS) (Gutierrez et al., 2010). Adding ferric chloride releases Fe^{3+} ions, reducing to Fe^{2+} ions where sulfide oxidizes to sulfur (Gutierrez et al., 2010; Yang & Bae, 2014). The released Fe^{2+} ions then precipitate out as FeS (Haaning Nielsen et al., 2005; Gutierrez et al., 2010; Yang & Bae, 2014), and Fe^{3+} ions precipitate out P as $FePO_4.2H_2O$ (Zhang et al., 2010; Yang & Bae, 2014).

As an emerging P recovery method, vivianite ($Fe_3(PO_4)_2.8H_2O$) is known to precipitate out from municipal wastewater in anaerobic systems (Rothe et al., 2016; Wilfert et al., 2018). Vivianite tends to precipitate out at neutral pH. Therefore, it tends to happen naturally as long as residual iron is present (Wu et al., 2019). One of the drawbacks of vivianite recovered from wastewater is that it tends to get trapped in the sludge (Wu et al., 2019; Robles et al., 2020). Various iron hydroxide minerals, such as lepidocrocite and ferrihydrite, and amorphous iron phosphate minerals are also known to precipitate out from wastewater dosed with iron (Wu et al., 2015).

2.4.2.1.2. Calcium phosphate recovery

Recovery of P as calcium phosphates is emerging as it is similar in structure to commercial phosphate fertilizers and has a high calcium content, giving it a higher potential to recover P (Lei et al., 2017; Law & Pagilla, 2018).

Most calcium phosphate precipitation occurs above a pH 9, and depending on the pH, different P species can be formed, such as hydroxyapatite, octa calcium phosphate, tricalcium phosphate (all at higher pH), and brushite (at near or below neutral pH) (Tran et al., 2014; Law & Pagilla, 2018). Other than pH, Ca/P molar ratio, temperature, and supersaturation level are key factors that determine the level of crystallinity in the formed mineral (Tran et al., 2014). Hydroxyapatite recovery is the most popular (Lei et al., 2017; Robles et al., 2020; Tran et al., 2014; Zheng et al., 2020), where recovering brushite leads to the development of the commercial CalPrex process (Law & Pagilla, 2018).

Research on the precipitation of calcium phosphate has been conducted using various coagulants, including calcium chloride addition (Tran et al., 2014) and calcium oxide (lime) addition (Hasegawa et al., 2017; Zheng et al., 2020), as well as relying on residual calcium in the

wastewater (Tervahauta et al., 2014; Lei et al., 2017). Using lime in wastewaters near neutral pH, the hydroxide ions produced will produce more alkaline conditions, increasing P precipitation efficiency (Zheng et al., 2020). Several studies have used lime for P recovery in municipal wastewater, but lime usage for swine wastewater is limited (Hasegawa et al., 2017; Zheng et al., 2020).

2.4.2.2. Use of recovered phosphorus in agriculture

Struvite precipitation has received the most attention regarding testing as a P fertilizer out of all the wastewater recovery processes being researched. Struvite supplies three nutrients essential to plant growth, allows the pH to increase naturally, and has frequently been reported to perform as well as more conventional acidulated fertilizer products when ground and blended into soils (Le Corre et al., 2009; Sengupta & Pandit, 2011; Antonini et al., 2012; Ackerman et al., 2013; Degryse et al., 2017;). However, when applied as granules, the performance is often compromised (Ackerman et al., 2013; Talboys et al., 2016; Degryse et al., 2017; Everaert et al., 2017).

The effectiveness of struvite granules appears to be greatly dependent upon soil conditions, the cropping system, and the production method (Antonini et al., 2012; Talboys et al., 2016; Degryse et al., 2017; Everaert et al., 2017). Dissolution also appears to be accelerated by soils with high sorption capacity (Degryse et al., 2017; Everaert et al., 2017). Degryse et al., 2017 documented that grinding struvite produced comparable biomass to MAP in an acid soil, suggesting that particle size be seriously considered when applying this product under acidic conditions. According to Talboys et al., 2016, only roughly a third of struvite granules dissolved in an Eutric Cambisol (pH 6.0) in a 90-day spring wheat experiment, could be physically

recovered, while TSP granules could not. Everaert et al., 2017 observed that struvite granules in a 100-day Petri dish incubation experiment showed less diffusion than MAP but greater lability in the soil < 8mm from the point of application. Ahmed et al., 2016 documented that struvite dissolution was observed when roots proliferated near the granule. Talboys et al., 2016 suggest that blending the more traditional granular fertilizers with struvite may provide early and late season release, which could be a way to integrate some of this waste stream recovery product into agricultural systems.

Detailed agronomic studies on iron and calcium phosphate products are limited. Only a smaller number of studies have looked at the agronomic effectiveness of calcium phosphate precipitates from wastes. The water solubility of the products is low, but citrate solubility is very high (> 90%), suggesting that their utility will be best under more acid conditions and/or in concert with plant root low molecular weight organic acid exudation (Szogi et al., 2012). Szogi et al., 2012 compared recovered Ca-P from swine and broiler manure to TSP and fresh broiler litter in vertical column studies filled with sandy, coastal plains soil and found that when applied at a high rate (170 kg P_2O_5 ha^{-1}), all were able to adequately supply P for cotton for the eight-week trial and P uptake and biomass exhibited no significant difference. Plant availability of recycled P products derived from dairy effluents and pig manures was evaluated using pot and soil incubation experiments by Achat et al., 2014. The final quality of these recovered products is affected by the presence of suspended particles, heavy metals, and other impurities, and it is essential to remove the suspended particles before chemical addition to produce high-quality products (Ping et al., 2016). The evidence is convincing that these products can play a role in supplying P nutrition. However, identifying the systems where they will be most effective is essential.

2.5. Phosphorus usage in agriculture and environmental quality

It is a great challenge to the agricultural community to balance increasing production while minimizing negative environmental impacts (Srivastava et al., 2016). Agriculture is crucial to the economy in the United States, making up 5.5% of the gross domestic product (GDP) and 10% of exports (USDA ERS, 2017). Agricultural production has been identified as a critical source of sediment, N, and P pollution, leading to the degradation of surface-water quality (Sharpley & Tunney, 2000; Chislock et al., 2013; Smith et al., 2017). These nutrients are released to the water bodies and then taken up by phytoplankton, resulting in excessive growth, known as algal blooms (Chislock et al., 2013; Carpenter et al., 2018). Algal blooms lead to anthropogenic eutrophication, limit light penetration, increase pH levels, deplete dissolved inorganic carbon, and suffocate other aquatic organisms due to oxygen depletion (Chislock et al., 2013). The toxic nature of the harmful algal blooms (HABs) is expected to intensify under future climate conditions due to the toxic cyanobacteria's ability to thrive in low light, warm, stagnant, nutrient-rich conditions (Paerl & Paul, 2012; Reichwaldt & Ghadouani, 2012).

The increase in P pollution to surface water is especially detrimental, although not exclusive, to freshwater bodies (Moody, 2011). It has been estimated that up to 70% of all surface-water inputs of P can be associated with non-point agricultural sources (Havlin et al., 2005). Controlling non-point P pollution is not a localized challenge, and global net P storage for both aquatic and terrestrial ecosystems has increased by over 75%, relative to pre-industrial levels, primarily due to P-based fertilizer application in agricultural soils (Bennet et al., 2001; Zhou et al., 2017).

The intensification of climate change is also causing significant problems in agricultural production, including drought and environmental concerns such as eutrophication (Zare et al.,

2016; Carpenter et al., 2018). Several climate models predict that global temperatures will continue to rise, leading to more intense storms and extended periods of drought. (Reichenwaldt & Ghadouani, 2012; Paerl et al., 2014). The runoff characteristics are influenced by rainfall intensity and soil infiltration (Kleinman et al., 2006). Moreover, precipitation extremes have a significant log-linear relationship with P loading, where a handful of significant rainfall events produce most of the P load in runoff (Carpenter et al., 2018). Fraser et al., 1999 documented that under conventional tillage, an increase in rainfall intensity from 1 mm to 10 mm h^{-1} can cause an increase in sediment, particulate P, and dissolved reactive P.

Moreover, studies conducted by Bostrom et al., 1988 and Okubo et al., 2012 found that many forms of recalcitrant P in sediment, such as apatite, which were once thought to be unavailable to biota, can be utilized by cyanobacteria. In addition, organic P, which is often considered resistant to degradation, has been found to contribute to algal growth by releasing orthophosphate from enzyme hydrolysis of organic molecules or direct uptake of organic P (Turner et al., 2002; Wang et al., 2007).

The eutrophication caused by P runoff is a severe problem for many communities. A study by Dodds et al., 2009 estimated that the increased water treatment costs due to harmful algal blooms and eutrophication could be as much as 2.4-4.6 billion U.S. dollars annually. In addition, the aesthetic value of surface waters may decrease due to eutrophication, which could negatively impact recreational and property values (Dodds, 2002; Krysel et al., 2003). Pollution from agricultural production is a persistent and complex problem despite increased research and mitigation techniques (Paerl et al., 2014; Dodd & Sharpley, 2016; Jarvie et al., 2017).

2.6. Agricultural management practices and phosphorus

As many soils are inherently low in readily plant-available P, producers regularly apply P-based fertilizers to help maximize crop yields (Hart & Quin, 2004). Agricultural cropping systems and management practices mainly impact agricultural nutrient loss (Liu et al., 2014a). To address environmental concerns such as erosion, nutrient loss, and water pollution, the United States Department of Agriculture Natural Resources Conservation Service (USDA-NRCS) promotes conservation practices designed to reduce erosion and pollution while improving soil health. This shift to emphasize soil health and conservation management techniques includes changes in tillage practices and planting cover crops (NRCS, 2015; Dodd & Sharpley, 2016). Conservation tillage and cover crops have improved soil health by reducing erosion, N and P loss, increasing soil organic matter, and improving aggregate stability (Hanrahan et al., 2018; Simeone et al., 2020).

No-till improves soil health by reducing the mechanical mixing of soil from conventional tillage, thereby preserving the aggregate structure and sequestering C in soil (Ogle et al., 2011). Good aggregation promotes an optimal balance of air and water in the soil, promotes microbial activity and diversity, and reduces the potential for soil particles to succumb to erosive forces (Blanco-Canqui et al., 2011). No-till has been shown to reduce sediment in the runoff by up to 80% in multiple ecoregions around the globe (Smith et al., 2015; TerAvest et al., 2015).

One of the most frequently suggested agricultural best management practices (BMPs) to decrease P loss is to encourage residue retention of crops on the soil surface and to add a cover crop during the typical fallow period (Dabney et al., 2001; Dumanski et al., 2006). Cover crops, defined as living ground cover sown after, during, or prior to a primary cash crop, are terminated before planting the following cash crop (Hartwig & Ammon, 2002). Several benefits of cover

crops have been documented, such as reduced soil erosion, slow surface runoff, decreased nutrient leaching and runoff, improved soil aggregate stability, and increased soil water storage (Dabney et al., 2001; DeBaets et al., 2011; Loss et al., 2015; Ruffati et al., 2019).

The 4R Nutrient Stewardship is a method of fertilizer management that minimizes potential losses of applied nutrients by adding the right source of nutrients at the right place, rate, and time (Bruulsema et al., 2009). The P fertilizers placed below the soil surface showed a reduction in both total P and dissolved P losses in surface runoff compared to the surface application of P fertilizers (Zeimen et al., 2006; Kimmel et al., 2001; Yuan et al., 2018; Wiens et al., 2019). In addition, it is documented that applying P fertilizer during high precipitation generally increases P loss (Sims & Kleinman, 2005; Vadas et al., 2008, 2011). Therefore, additional information about the interaction between cover crops and P fertilizer management and the effects on P loss is needed to develop agricultural BMPs further to mitigate P loss.

2.6.1. Phosphorus management practices and phosphorus losses

Mitigating P loss is difficult as P loss occurs in both dissolved and particulate-bound forms. Therefore, BMPs targeting particulate-bound and dissolved P pathways are needed to mitigate P loss. This is best accomplished by developing management practices targeting P source and transport factors.

Many fertilizer recommendation systems were developed when extensive tillage was more common, and the recommendations are based on plant available P within the plow layer using field studies (Smith et al., 2017). Research has documented an increase of dissolved reactive P (DRP) in runoff events as a function of water-soluble P (WSP) in fertilizer sources such as TSP (79% WSP) and swine manure (70% WSP) (Kleinman et al., 2006; Shigaki et al., 2007; Shigaki & Sharpley, 2011). Shigaki et al., 2007 also documented the importance of the

degree of water solubility of the P source and rainfall intensity on P transportation. Concentrations of DRP loss at 2.5 cm h^{-1} were 28.21 mg L^{-1} from TSP compared to 0.25 mg L^{-1} from rock phosphate (Shigaki et al., 2007).

Fluid fertilizers showed a lower nutrient loss than dry, granular fertilizers (Smith et al., 2017). Smith et al., 2017 also showed that applying fluid polyphosphate on the surface decreased soluble P losses by 98% compared to applying granular monoammonium phosphate and diammonium phosphate fertilizers. A well-known mechanism to reduce potential P loss in surface runoff is incorporating surface-applied P-based fertilizers by tillage (Sharpley & Smith, 1991; Smith et al., 1991). According to Kimmel et al., 2001 subsurface application of P-based fertilizer in no-till conditions decreased bioavailable P losses by 70% compared to broadcast application. Additionally, the subsurface application has increased P use efficiency, P uptake, and grain yield compared to surface broadcast in no-till systems (Hairston et al., 1990). However, surface broadcast application of P fertilizer is still the most widely used strategy for no-till corn-soybean rotations in much of the Great Plains due to its low cost and ease of use (Mallarino et al., 2009).

On the other hand, soil stratification and P accumulation at the soil surface have been identified as possible reasons that no-till has not been more effective (Smith et al., 2015; Dodd & Sharpley, 2015; Smith et al., 2017; Jarvie et al., 2017). In no-till management, P fertilizer is often broadcast on the soil surface, concentrating the nutrient in the top few mm of soil due to the lack of mechanical incorporation, where surface water interacts most (Sims et al., 2000). Smith et al., 2017 found that injecting liquid polyphosphate fertilizer had less soluble and total P loss than annual and biannual surface broadcasting in no-till fields. Sharpley, 2003 found that tilling

manured soils can reduce P stratification. Smith et al., 2017 demonstrated that disking had the opposite effect, increasing the amount of stratification.

2.6.2. Cover crops and phosphorus losses

The addition of a cover crop during a usually fallow period increases carbon storage in soils, improves soil aggregate stability, and decreases adverse effects of wind and water erosion (Reicosky & Forcella, 1998; Battany & Grismer, 2000; Hallett et al., 2003). Implementing a cover-cropped system keeps the soil surface under a permanent layer of vegetative cover, offering benefits such as reducing interrill and splash erosion and protecting soil aggregates and compaction of topsoil (Kaspar et al., 2001; Morgan, 2005). Sediment losses with cover crops reduce up to 100% sediment losses compared to fields with no cover crops (Blanco-Canqui, 2018). However, the effects of cover crops on P loss are inconsistent, sometimes resulting in more significant P loss and sometimes less P loss compared to no cover. (Aronsson et al., 2016; Christianson et al., 2017; Baulch et al., 2019).

Besides these benefits, cover crops make P more bioavailable (Teboh & Frazen, 2011; Dodd & Sharpley, 2015). Cover crops, such as fava beans, buckwheat, and white lupine can have high P uptake efficiency and access fractions not available to cash crops (Horst et al., 2001; Eichler-Lobermann et al., 2008; Teboh & Frazen, 2011). They can excrete mineral P solubilizing compounds and organic P hydrolyzing enzymes and improve microorganism activity that can increase the volume of soil explored and compounds excreted that increase P availability, frequently over their own needs (Eichler, 2004; Richardson & Simpson, 2011). Cover crops moved P to the soil surface, making it more accessible to plants through the relationships with mycorrhizal fungi, secreting root exudates that solubilize P or altering root architecture (Hallama

et al., 2019). Cover crops have also been shown to increase microbial biomass P via increasing microbial activity in soils (Hallama et al., 2019; Starr, 2021).

Cover crops may accumulate significant P within the cover crop tissue as a P source when growing and developing, which can impact water quality through surface runoff (Liu et al., 2014b; Carver et al., 2021). It is crucial to preserve the assimilated P within the crop tissue to minimize this impact (Liu et al., 2014b, 2019), influenced by various management factors, including selecting the cover crop species and termination method (Carver et al., 2020). After cover crop termination, the decomposing organic matter can provide readily bioavailable P to microbes, which becomes mineralized and available for crops (Dabney, 1998; Eichler-Lobermann et al., 2008). Eichler-Lobermann et al., 2008 determined that P mobilization from cover crop growth was the primary mechanism of increased P availability in their study rather than the decomposing plant material. It has been suggested that the presence of plant residue at the surface and in root biomass (consisting of 7-86% P) is readily available after freeze-thaw cycles and may contribute to DRP in runoff and leachate (Liu et al., 2013). After these cycles, dead plant cells can spill the available P onto soil surfaces. Macropores left by the root growth and improved aggregation can create preferential pathways for the loss of the labile P (Liu et al., 2014a). Although increased bioavailability of P from cover crops could benefit crop yields and reduce dependence on inorganic fertilizer, it may have negative consequences if availability does not coincide with need (Eichler-Lobermann et al., 2008; Dodd & Sharpley, 2015). Detailed characterization of soil and P pools in different agricultural systems, with and without cover crops, may provide better insight into the cover crop effect on P mobility.

References

Achat, D. L., M. Sperandio, M. L. Daumer, A.C. Santellani, L. Prud'Homme, M. Akhtar, and C. Morel. 2014. Plant-availability of phosphorus recycled from pig manures and dairy effluents as assessed by isotopic labeling techniques. Geoderma. 232–234: 24–33.

Ackerman, J.N., F. Zvomuya, N. Cicek, and D. Flaten. 2013. Evaluation of manure-derived struvite as a phosphorus source for canola. Can. J. Plant Sci. 93:419-424.

Ahmed, S., T.N. Klassen, S. Keyes, M. Daly, D.L. Jones, M. Mavrogordato, I. Sinclair, and T. Roose. 2016. Imaging the interaction of roots and phosphate fertiliser granules using 4D x-ray tomography. Plant Soil. 401:125-134.

Ajiboye, B., O. O. Akinremi, Y. Hu and D.N. Flaten. 2007. Phosphorus speciation of sequential extracts of organic amendments using nuclear magnetic resonance and X-ray absorption near-edge structure spectroscopy. J. Environ. Qual. 36:1563-1576.

Ajiboye, B., O.O. Akinremi, Y. Hu and A. Jurgensen. 2008. XANES speciation of phosphorus in organically amended and fertilized Vertisol and Mollisol. Soil Sci. Soc. Am. J. 72:1256-1262.

Ali, A., Y.W. Chiang, and R.M. Santos. 2022. X-ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions. Minerals. 12: 205. https://doi.org/10.3390/min12020205

Antonini, S., M.A. Arias, T. Eichert, and J. Clemens. 2012. Greenhouse evaluation and environmental impact of different urine-derived struvite fertilizers as phosphorus sources for plants. Chemosphere. 89:1202-1210.

Aronsson, H., E.M. Hansen, I.K. Thomsen, J. Liu, A.F. Øgaard, H. Känkänen, and B. Ulén. 2016. The ability of cover crops to reduce nitrogen and phosphorus losses from arable land in southern Scandinavia and Finland. J. Soil Water Conserv. 71:41-55.

Bashar, R., K. Gungor, K. G. Karthikeyan, and P. Barak. 2018. Cost effectiveness of phosphorus removal processes in municipal wastewater treatment. Chemosphere. 197: 280–290. https://doi.org/10.1016/j.chemosphere.2017.12.169

Batstone, D. J., and B. Virdis. 2014. The role of anaerobic digestion in the emerging energy economy. Current Opinion in Biotechnology. Elsevier. 27: 142–149.

Battany, M., and M.E. Grismer. 2000. Rainfall runoff and erosion in Napa Valley vineyards: effect of slope, cover, and surface roughness. Hydrol. Process. 14:1289-1304

Baulch, H.M., J.A. Elliott, M.R.C. Cordeiro, D.N. Flaten, D.A. Lobb, and H.F. Wilson. 2019. Soil and water management practices: Opportunities to mitigate nutrient losses to surface waters in the northern Great Plains. Environ. Rev. 27: 447-477. https://doi.org/10.1139/er-2018-0101

Beauchemin, S., D. Hesterberg, J. Chou, M. Beauchemin, R.R. Simard and D.E. Sayers. 2003. Speciation of phosphorus in phosphorus-enriched agricultural soils using X-ray absorption near-edge structure spectroscopy and chemical fractionation. J. Environ. Qual. 32:1809–1819.

Bennett E.M., S.R. Carpenter, and N.F. Caraco. 2001. Human impact on erodible phosphorus and eutrophication: a global perspective. Bioscience. 51:227–234.

Blackwell, M., T. Darch, and R. Haslam. 2019. Phosphorus use efficiency and fertilizers: future opportunities for improvements, Front Agric Sci Eng. 6: 332–340.

Blanco-Canqui, H. 2018. Cover crops and water quality. Agron. J. 110:1633– 1647.

Blanco-Canqui, H., M.M. Mikha, D.R. Presley, and M.M. Claassen. 2011. Addition of cover crops enhances no-till potential for improving soil physical properties. J. Soil Water Conserv. 75: 1471-1482.

Boström, B., G. Persson, and B. Broberg. 1988. Bioavailability of different phosphorus forms in freshwater systems. Hydrobiologia, 170: 133-155.

Bowers, K.E., T. Zhang, and J.H. Harrison. 2007. Phosphorus removal by struvite crystallization in various livestock wastewaters. In: Proceedings of International Symposium on Air Quality and Waste Management for Agriculture. American Society of Agricultural and Biological Engineers Meeting Paper No. 701P0907cd. St. Joseph, Mich., ASABE.

Brady N. C., and R. R. Well. 2002. The nature and properties of soil. Pearson Education, Inc., NJ.

Bruulsema, T., J. Lemunyon, and B. Herz. 2009. Know your fertilizer rights. Crops and Soils. 42:13-16.

Bu, F., S. Du, L. Xie, R. Cao, and Q. Zhou. 2017. Swine manure treatment by anaerobic membrane bioreactor with carbon, nitrogen and phosphorus recovery. Water Sci. Technol. 76: 1939–1949. https://doi.org/10.2166/wst.2017.278

Carman, R., G. Edlund and C. Damberg. 2000. Distribution of organic and inorganic phosphorus compounds in marine and lacustrine sediments: A P-31 NMR study. Chem. Geol. 163:101-114.

Carpenter, S.R., E.G. Booth, and C.J. Kucharik. 2018. Extreme precipitation and phosphorus loads from two agricultural watersheds. Limnol. Oceanogr. 63:1221–1233.

Carver, R.E., N. O. Nelson, K. L. Roozeboom, G. J. Kluitenberg, P. J. Tomlinson, Q. Kang, and D. S. Abel. 2022. Cover crop and phosphorus fertilizer management impacts on surface water quality from a no-till corn-soybean rotation, J. Environ. Manage., 301: 113818. https://doi.org/10.1016/j.jenvman.2021.113818.

Carver, R.E., N.O. Nelson, K.L. Roozeboom, and M.B. Kirkham. 2020. Species and termination method effects on phosphorus loss from plant tissue. J. Environ. Qual. 49:97–105.

Chang, S.C., and M.L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci. 84:133-144.

Cheng, D., H.H Ngo, W. Guo, S.W. Chang, D.D. Nguyen, Q.A. Nguyen, J. Zhang, and S. Liang. 2021. Improving sulfonamide antibiotics removal from swine wastewater by supplying a new pomelo peel derived biochar in an anaerobic membrane bioreactor. Bioresour. Technol. 319: 124160–124160. https://doi.org/10.1016/j.biortech.2020.124160

Cheng, H.-H., B. Narindri, H. Chu, and L.M. Whang. 2020. Recent advancement on biological technologies and strategies for resource recovery from swine wastewater. Bioresour. Technol. 303: 122861–122861. https://doi.org/10.1016/j.biortech.2020.122861

Chislock, M. F., E. Doster, R.A. Zitomer, and A.E. Wilson. 2013. Eutrophication: Causes, consequences, and controls in aquatic ecosystems. Nature Education Knowledge, 4(4),10.

Christianson R., J. Fox, C. Wong, D. Caraco, A. Daniels, N. Law, and B. Stack. 2017. Literature review and synthesis of the effectiveness of cover crops for water quality management in the upper Mississippi river basin (White Paper). Center for Watershed Protection, Inc., Ellicott City, Maryland.

Cordell, D., and T.S. Neset. 2014. Phosphorus vulnerability: a qualitative framework for assessing the vulnerability of national and regional food systems to the multidimensional stressors of phosphorus scarcity. Glob. Environ. Change. 24: 108–122.

Cornel, P., and C. Schaum. 2009. Phosphorus recovery from wastewater: Needs, technologies and costs. Water Sci. Technol. 59: 1069–1076. https://doi.org/10.2166/wst.2009.045

Dabney, S. M. 1998. Cover crop impacts on watershed hydrology. J Soil Water Conserv. 53: 207-215.

Dabney, S., J. Delgado, and D. Reeves, D. 2001. Using winter cover crops to improve soil and water quality. Commun Soil Sci Plant Anal. 32:221–1250.

De Baets, S., J. Poesen, J. Meersmans, and L. Serlet, L. 2011. Cover crops and their erosion reducing effects during concentrated flow erosion. Catena. 85:237–244.

Degryse, F., R. Baird, R.C. da Silva, and M.J. McLaughlin. 2017. Dissolution rate and agronomic effectiveness of struvite fertilizers – effect of soil pH, granulation and base excess. Plant Soil. 410:139-152.

Dodd, R. J., and A.N. Sharpley. 2015. Recognizing the role of soil organic phosphorus in soil fertility and water quality. Resour Conserv Recycl. 105: 282-293.

Dodd, R. J., and A.N. Sharpley. 2016. Conservation practice effectiveness and adoption: unintended consequences and implications for sustainable phosphorus management. Nutr. Cycling Agroecosyst. 104: 373-392.

Dodds, W. K. 2002. Freshwater Ecology: Concepts and Environmental Applications; Academic Press: San Diego, CA.

Dodds, W. K., W.W. Bouska, J.L. Eitzmann, T.J. Pilger, K.L. Pitts, A.J. Riley, J.T. Schloesser, and D.J. Thornbrugh. 2009. Eutrophication of U.S. Freshwaters: Analysis of potential economic damages. Environ. Sci. Technol. 43: 12-19.

Duhamel, S., J.M. Diaz, J.C. Adams, K. Djaoudi, V. Steck, and E.M. Waggoner. 2021. Phosphorus as an integral component of global marine biogeochemistry. Nat. Geosci.14: 359–368.

Dumanski, J., R. Pieretti, J.R. Benites, D. McGarry, and C. Pieri. 2006. The paradigm of conservation agriculture. Proc. World Assoc. Soil and Water Conserv. P1:58-64.

Egle, L., H. Rechberger, and M. Zessner. 2015. Overview and description of technologies for recovering phosphorus from municipal wastewater. Resour Conserv Recycl. 105: 325–346. https://doi.org/10.1016/j.resconrec.2015.09.016

Eichler, B. 2004. Opportunities to influence the P cycle in sustainable Agroecosystems. Habilitation thesis [University of Rostock, Germany]. University of Rostock Research Database.

Eichler-Löbermann, B., S. Köhne, B. Kowalski, and E. Schnug. 2008. Effect of catch cropping on phosphorus bioavailability in comparison to organic and inorganic fertilization. J. Plant Nutr. 31: 659-676.

Encyclopedia Britannica. 2018. Sir Henry Gilbert. Encyclopedia Britannica. https://www.britannica.com/biography/Henry-Gilbert-British-chemist

Essington, M. E., 2015. Soil and Water Chemistry: An Integrative Approach. CRC press.

Evans, P. J., A. Doody, M. Harclerode, P. Vila, P. Parameswaran, K. Lim, J. Bae, C. Shin, P.H. Lee, A. Tan, P. Mccarty, W. Parker, K. Guy, M. Page, and S. Maga. 2018. Anaerobic Membrane Bioreactor (AnMBR) for Sustainable Wastewater Treatment. Project ER-201434. Department of Defense Environmental Security Technology Program Final Report.

Everaert, M., F. Degryse, M.J. McLaughlin, D. De Vos, and E. Smolders. 2017. Agronomic effectiveness of granulated and powdered P-exchanged Mg-Al LDH relative to struvite and MAP. J. Agric. Food Chem. 65:6736-6744.

Fendorf, S.E., and D.L. Sparks. 1996. X-ray absorption fine structure. p 378-416. *In* D.L. Sparks (ed.) Methods of soil analysis. Part. 3. SSSA, Madison, WI.

Fraser, A. I., T.R. Harrod, and P.M. Haygarth. 1999. The effect of rainfall intensity on soil erosion and particulate phosphorous transfer from arable soils. Water Sci. Technol. 39: 41-45.

Gungor, K., A. Jurgensen and K.G. Karthikeyan. 2007. Determination of phosphorus speciation in dairy manure using XRD and XANES spectroscopy. J. Environ. Qual. 36:1856-1863.

Gutierrez, O., D. Park, K.R. Sharma, and Z. Yuan. 2010. Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment. Water Res. 44: 3467–3475. https://doi.org/10.1016/j.watres.2010.03.023

Haaning Nielsen, A., P. Lens, J. Vollertsen, and T. Hvitved-Jacobsen. 2005. Sulfide–iron interactions in domestic wastewater from a gravity sewer. Water Res. 39: 2747–2755. https://doi.org/10.1016/j.watres.2005.04.048

Hagos, K., J. Zong, D. Li, C. Liu, and X. Lu. 2017. Anaerobic co-digestion process for biogas production : Progress , challenges and perspectives. Renew. Sust. Energ. Rev. 76: 1485–1496.

Hairston, J.E., W.F. Jones, and T.L. Gilbert. 1990. Tillage and fertilizer effects on soybean growth and yield on three Mississippi soils. J. Prod. Agric. 3:317-323.

Hallama, M., C. Pekrun, H. Lambers, and E. Kandeler. 2019. Hidden miners – the roles of cover crops and soil microorganisms in phosphorus cycling through agroecosystems. Plant Soil. 434:7-45.

Hallett, P.D., D.C Gordon, and A.G. Bengough. 2003. Plant influence on rhizosphere hydraulic properties: direct measures using a miniaturized infiltrometer. New Phytol. 157:597-603.

Hanrahan, B. R., J.L. Tanka, S.F. Christophera, U.H. Mahla, M.T. Trentmana, and T.V. Royer. 2018. Winter cover crops reduce nitrate loss in an agricultural watershed in the central U.S. Agric Ecosyst Environ. 265: 513-523.

Hansen, N.C., T.C. Daniel, A.N. Sharpley and J.L. Lemunyon. 2002. The fate and transport of phosphorus in agricultural systems. J. Soil Water Conserv. 57:408-417.

Harclerode, M., A. Doody, A. Brower, P. Vila, J. Ho, and P. J. Evans. 2020. Life cycle assessment and economic analysis of anaerobic membrane bioreactor whole-plant configurations for resource recovery from domestic wastewater. J. Environ. Manage. 269: 110720.

Harris W. and G.N. White. 2008. X-ray diffraction techniques for soil mineral identification. 81-115. In Ulery and Dress (ed.) Methods of soil analysis. Part. 5.SSSA, Madison, WI.

Hart, M.R. and B.F. Quin. 2004. Phosphorus runoff from agricultural land and direct fertilizer effects: A review. J. Environ. Qual. 33:1954-1972.

Hartwig, N. and H. Ammon. 2002. 50th anniversary - invited article - cover crops and living mulches. Weed Science. 50:688-699.

Hasegawa, T., Y. Kurose, and Y. Tanaka. 2017. Advanced treatment technique for swine wastewater using two agents: Thermally polymerized amorphous silica and hydrated lime for color and phosphorus removal and sulfur for nitrogen removal. Anim. Sci. J. 88(10): 1636–1643. https://doi.org/10.1111/asj.12803

Havlin, J.L., J.D. Beaton, S.L. Tisdale, and W.L. Nelson. 2005. Soil Fertility and Fertilizers: An Introduction to Nutrient Management. Vol. 515. Upper Saddle River, NJ: Pearson Prentice Hall.

Hedley, M.J., W.B. Stewart, and B.S. Chauhan. 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. Soil Sci. Soc. Am. J. 46:970-976.

Henze, M., M.C.M.van Loosdrecht, G.A. Ekama, and D. Brdjanovic. 2008. Biological Wastewater Treatment: Principles, Modelling and Design. IWA Publishing.

Heronemus, E., K. H.H. Gamage, G. M. Hettiarachchi, and P. Parameswaran. 2021. Efficient recovery of phosphorus and sulfur from Anaerobic Membrane Bioreactor (AnMBR) permeate using chemical addition of iron and evaluation of its nutrient availability for plant uptake. Sci. Total Environ. 783: 146850. https://doi.org/10.1016/j.scitotenv.2021.146850.

Hesterberg, D., W.Q. Zhou, K.J. Hutchison, S. Beauchemin, and D.E. Sayers. 1999. XAFS study of adsorbed and mineral forms of phosphate. J. Synchrotron Radiat. 6: 636-638.

Hettiarachchi, G.M., E. Lombi, M.J. McLaughlin, D. Chittleborough, and P. Self. 2006. Density changes around phosphorus granules and fluid bands in a calcareous soil. Soil Sci. Soc. Am. J. 70:960-966.

Hettiarachchi, G.M., M.J. McLaughlin, K.G. Scheckel, D.J. Chittleborough, M. Newville, S. Sutton, E. Lombi. 2008. Evidence for different reaction pathways for liquid and granular micronutrients in a calcareous soil. Soil Sci. Soc. Am. J. 72, 98–110.

Horst, W. J., M. Manh, J.M. Jibrin, and V.O. Chude. 2001. Agronomic measures for increasing P availability to crops. Plant Soil. 237, 211-223.

IPNI. 2010. Phosphorus fertilizer production and technology. (http://www.ipni.net/)

IUPAC Recommendations 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and Methodological approaches. https://publications.iupac.org/pac/2000/pdf/7208x1453.pdf

Jarvie, H. P., L.T. Johnson, A.N. Sharpley, D.R. Smith, D.B. Baker, T.W. Bruulsema, and R. Confesor. 2017. Increased soluble phosphorus loads to Lake Erie: Unintended consequences of conservation practices?. J. Environ. Qual. 46: 123-132.

Jupp, A. R., S. Beijer, G.C. Narain, W. Schipper, and J.C. Slootweg. 2021. Phosphorus recovery and recycling–closing the loop. Chem Soc Rev. 50(1): 87–101.

Kannan, A. D., P. Evans, and P. Parameswaran. 2020. Long-term microbial community dynamics in a pilot-scale gas sparged anaerobic membrane bioreactor treating municipal

wastewater under seasonal variations. Bioresour. Technol. 310: 123425–123425. https://doi.org/10.1016/j.biortech.2020.123425

Kashem, M.A., O.O. Akinremi and G.J. Racz. 2004. Phosphorus fractions in soil amended with organic and inorganic phosphorus sources. Can. J. Soil Sci. 84:83-90.

Kaspar, T.C., J.K. Radke, and J.M. Lflen. 2001. Small grain cover crops and wheel traffic effects on infiltration, runoff, and erosion. J. Soil Water Conserv. 56:160-164.

Kelly, S. D., D. Hesterberg, and B. Ravel. 2008. Analysis of soils and minerals using X-ray absorption spectroscopy in Method of Soil Analysis, Part 5 (Soil Sci. Soc. Am., Madison, 2008). 387–464.

Kimmell, R.J., G.M. Pierzynski, K.A. Janssen, and P.L. Barnes. 2001. Effects of tillage and phosphorus placement on phosphorus runoff losses in a grain sorghum-soybean rotation. J. Environ. Qual. 30:1324-1330.

Kizewski, F., Y.T. Liu, A. Morris, and D. Hesterberg. 2011. Spectroscopic approaches for phosphorus speciation in soils and other environmental systems. J. Environ. Qual. 40:751–766.

Kleinman, P. J., M.S. Srinivasan, C.J. Dell, and J.P. Schmidt. 2006. Role of rainfall intensity and hydrology in nutrient transport via surface runoff. J. Environ. Qual. 35(4): 1248-59.

Klug, H.P. and L. E. Alexander. 1974. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. John Wiley & Sons, New York.

Kruse, J., and P. Leinweber. 2008. Phosphorus in sequentially extracted fen peat soils: A K-edge X-ray absorption near-edge structure (XANES) spectroscopy study. J. Plant Nutr. and Soil Sci. 171:613-620.

Krysel, C., E.M. Boyer; C. Parson, P. Welle. 2003. Lakeshore Property Values and Water Quality: Evidence from Property Sales in the Mississippi Headwaters Region; Submitted to the Legislative Commission on Minnesota Resources: St. Paul, MN. 59.

Law, K. P., and K.R. Pagilla. 2018. Phosphorus Recovery by Methods Beyond Struvite Precipitation. Water Environ. Res. 90(9): 840–850. https://doi.org/10.2175/106143017X15131012188006

Le Corre, K.S., E. Valsami-Jones, P. Hobbs, and S.A. Parsons. 2009. Phosphorus recovery from wastewater by struvite crystallization: A Review. Crit Rev Environ Sci Technol. 39:433-477.

Lei, Y., B. Song, R.D. van der Weijden, M. Saakes, and C.J.N. Buisman. 2017. Electrochemical Induced Calcium Phosphate Precipitation: Importance of Local pH. Environ. Sci. Technol. 51(19): 11156–11164. https://doi.org/10.1021/acs.est.7b03909

Leikam, D. F., and F.P. Achorn. 2005. Phosphate fertilizers: Production, characteristics, and technologies. In Sims, J.T., and A. Sharpley. (eds.) Phosphorus: Agriculture and the Environment. Agron. Monogr. 46. ASA, CSSA, and SSSA, Madison, WI.

Li, W., S. R. Joshi, S. Hou, D. J. Burdige, D. L. Sparks, and D. P. Jaisi. 2015. Characterizing Phosphorus Speciation of Chesapeake Bay Sediments Using Chemical Extraction, 31P NMR, and X-ray Absorption Fine Structure Spectroscopy. Environ. Sci. Technol. 49 (1): 203-211.

Liao, B. Q., J. T. Kraemer, and D. M. Bagley. 2006. Anaerobic membrane bioreactors: Applications and research directions. Crit Rev Environ Sci Technol. 36(6): 489–530.

Lim, K., P. J. Evans, and P. Parameswaran. 2019. Long-Term Performance of a Pilot-Scale Gas-Sparged Anaerobic Membrane Bioreactor under Ambient Temperatures for Holistic Wastewater Treatment. Environ. Sci. Technol. 53(13): 7347–7354. https://doi.org/10.1021/acs.est.8b06198

Lin, H., W. Peng, M. Zhang, J. Chen, H. Hong, and Y. Zhang. 2013. A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives. Desalination. 314: 169–188.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Liu, J. R., R. Khalaf, B. Ule'n, and G. Bergkvist. 2013. Potential phosphorus release from catch crop shoots and roots after freeze-thawing. Plant Soil. 371: 543-557.

Liu, J., B. Ulen, G. Bergkvist, and H. Aronsson. 2014. Freeze-thawing effects on phosphorus leaching from catch crops. Nutr. Cycling Agroecosyst. 99: 17-30.

Liu, J., G. Bergkvist, and B. Ulen. 2014a. Biomass production and phosphorus retention by catch crops on clayey soils in southern and central Sweden. Field Crops Res. 171:130-137.

Liu, J., J. Yang, B.J. Cade-Menun, X. Liang, Y. Hu, C.W. Liu, Y. Zhao, L. Li, and J. Shi. 2013. Complementary phosphorus speciation in agricultural soils by sequential fractionation, solution 31P nuclear magnetic resonance, and phosphorus K-edge X-ray absorption near edge structure spectroscopy. J. Environ. Qual. 42: 1763−1770.

Liu, J., M.L. Macrae, J.A. Elliott, H.M. Baulch, H.F. Wilson, and P.J.A. Kleinman. 2019. Impacts of cover crops and crop residues on phosphorus losses in cold climates: A review. J. Environ. Qual. 48(4): 850–868.

Lombi E., G.M. Hettiarachchi, and K.G. Scheckel. 2011. Advanced in situ spectroscopic techniques and their applications in environmental biogeochemistry: Introduction to the special section. J. Environ. Qual. 40: 659-666.

Lombi, E., K.G. Scheckel, R.D. Armstrong, S. Forrester, J.N. Cutler and D. Paterson. 2006. Speciation and distribution of phosphorus in a fertilized soil: A synchrotron-based investigation. Soil Sci. Soc. Am. J. 70: 2038–2048.

Lombi, E., M.J. McLaughlin, C. Johnston, R.D. Armstrong, and R.E. Holloway. 2004. Mobility and Lability of phosphorus from granular and fluid Monoammonium phosphate differs in a calcareous soil. Soil Sci. Soc. Am. J. 68: 682–689.

Loss A., A. Brass, B.S. Oliveira, L.P. Koucher, R.A. Oliveiria, C. Kurtz, P.E. Lovato, P. Curmi, G. Brunetto, and J.J. Comim. 2015. Total organic carbon and soil aggregation under a no-tillage agroecological system and conventional tillage system for onion. Rev. Bras. Cienc Solo. 39: 1212-1224.

Mallarino, A.P., S.R. Barcos, J.R. Prater, and D.J Wittry. 2009. Timing of broadcast phosphorus fertilizers for no-till corn and soybeans. Soi Sci. Soc. Am. J. 73: 2143-2150.

Massey, M.S., 2019. X-ray spectroscopic quantification of Struvite and Dittmarite recovered from wastewater. J. Environ. Qual. 48: 193–198.

Massey, M.S., I. Zohar, J.A. Ippolito, and M.I. Litaor. 2018. Phosphorus sorption to aluminum based water treatment residuals reacted with dairy wastewater: 2. X-ray Absorption Spectroscopy. J. Environ. Qual. 47: 546–553.

Massey, M.S., J.A. Ippolito, J.G. Davis, and R.E. Sheffield. 2010. Macroscopic and microscopic variation in recovered magnesium phosphate materials: implications for phosphorus removal processes and product re-use. Bio resour. Technol. 101: 877–885.

Mayer, B. K., L.A. Baker, T.H. Boyer, P. Drechsel, M. Gifford, M.A. Hanjra, P. Parameswaran, J. Stoltzfus, P. Westerhoff, and B.E. Rittmann. 2016. Total Value of Phosphorus Recovery. Environ. Sci. Technol. 50(13): 6606–6620. https://doi.org/10.1021/acs.est.6b01239

McBeath, T.M., E. Lombi, M.J. McLaughlin, and E.K. Bunemann. 2009. Exchangeability of orthophosphate and pyrophosphate in soils: a double isotopic labelling study. Plant Soil. 314: 243-252.

McBeath, T.M., R.J. Smernik, E. Lombi, and M.J. McLaughlin. 2006. Hydrolysis of pyrophosphate in a highly calcareous soil: a solid-state phosphorus-31 NMR Study. Soil Sci. Soc. Am. J. 70: 856-862.

McCarty, P. L., J. Bae, and J. Kim. 2011. Domestic wastewater treatment as a net energy producer - can this be achieved?. Environ. Sci. Technol. 45(17): 7100–6.

Meinen, R. J., K.B. Kephart, and R.E. Graves. 2014. Economic feasibility and evaluation of a novel manure collection and anaerobic digestion system at a commercial swine finisher enterprise. Biomass Bioenergy. 63: 10–21. https://doi.org/10.1016/j.biombioe.2014.01.032

Milani, N., G.M. Hettiarachchi, D.G. Beak, M. J. McLaughlin, J. K. Kirby, and S. P. Stacey. 2015. Fate of zinc oxide nanoparticles coated onto macronutrient fertilizers in an alkaline calcareous soil. PLoS One 10(5): e0126275.

Montalvo, D., F. Degryse, and M.J. McLaughlin. 2014. Fluid fertilizers improve phosphorus diffusion but not lability in Andisols and Oxisols. Soil Sci. Soc. Am. J. 78: 214-224.

Moody, P. W. 2011. Environmental risk indicators for soil phosphorus status. Soil Res. 49: 247-252.

Moore, D. M. and R.C. Reynolds, Jr. 1997. X-Ray Diffraction and the Identification and Analysis of Clay Minerals (Second Edition). Oxford University Press. NY.

Morgan, R.P.C. 2005. Soil erosion and conservation. Blackwell Science Ltd. Oxford.

Nelson, N. O., R.L. Mikkelsen, and D.L. Hesterberg. 2003. Struvite precipitation in anaerobic swine lagoon liquid: Effect of pH and Mg:P ratio and determination of rate constant. Bioresour. Technol. 89(3): 229–236. https://doi.org/10.1016/S0960-8524(03)000762

NRCS. 2015. Soil health literature summary – Effects of conservation practices on soil properties in areas of crop land. Natural Resources Conservation Service, National Soil Survey Center. United States Department of Agriculture.

Ogle, S. M., A. Swan, and K. Paustian. 2011. No-till management impacts on crop productivity, carbon input and soil carbon sequestration. Agric. Ecosyst. Environ. 149: 37-49.

Okubo, Y., T. Inoue, and K. Yokota. 2012. Estimating bioavailability of soil particulate phosphorus to Microcystis aeruginosa. J. Appl. Phycol. 24: 1503-1507.

Otoo, M., P. Drechsel, and M.A. Hanjra. 2015. Business Models and Economic Approaches for Nutrient Recovery from Wastewater and Fecal Sludge. Springer. 247–268. https://doi.org/10.1007/978-94-017-9545-6_13

Paerl, H. W., and V.J. Paul. 2012. Climate change: Links to global expansion of harmful cyanobacteria. Water Res. 46: 1349-1363.

Paerl, H. W., N.S. Hall, B.L. Peierls, and K.L. Rossignol. 2014. Evolving paradigms and challenges in estuarine and coastal eutrophication dynamics in a culturally and climatically stressed world. Estuaries and Coast. 37: 243-258.

Pastor, L., D. Mangin, J. Ferrer, and A. Seco. 2010. Struvite formation from the supernatants of an anaerobic digestion pilot plant. Bioresour. Technol. 101(1): 118–125. https://doi.org/10.1016/j.biortech.2009.08.002

Peak, D., J.T. Sims and D.L. Sparks. 2002. Solid-state speciation of natural and alum-amended poultry litter using XANES spectroscopy. Environ. Sci. Technol. 36: 4253-4261.

Pierzynski, G.M., R.W. McDowell, and J.T. Sims. 2005. Chemistry, cycling, and potential movement of inorganic phosphorus in soils. In J. Sims and A. Sharpley, (eds.) Phosphorus: Agriculture and the environment. ASA, CSSA, SSSA, Madison, WI.

Pierzynski, G.M., T.J. Logan, S. J. Traina, and J.M. Bigham. 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils: Descriptions of phosphorus rich materials. Soil Sci. Soc. Am. J. 54: 1583-1589.

Pierzynski, J. and G.M. Hettiarachchi. 2018. Reactions of phosphorus fertilizers with and without a fertilizer enhancer in three acidic soils with high phosphorus-fixing capacity. Soil Sci. Soc. Am. J. 82:1124-1139.

Ping, Q., Y. Li, X. Wu, L.U. Yang, and L. Wang. 2016. Characterization of morphology and component of struvite pellets crystallized from sludge dewatering liquor: Effects of total suspended solid and phosphate concentrations. J. Hazard. Mater. 310: 261–269.

Qiu, M., A. Singh, D. Wang, J. Qu, M. Swihart, H. Zhang, and P.N. Prasad. 2019. Biocompatible and biodegradable inorganic nanostructures for nanomedicine: Silicon and black phosphorus. Nano Today. 25: 135–155.

Reichenwaldt, E. S., and A. Ghadouani. 2012. Effects of rainfall patterns on cyanobacterial blooms in a changing climate: Between simplistic scenarios and complex dynamics. Water Res. 40: 1372-1393.

Reicosky, D.C., and F. Forcella. 1998. Cover crops and soil quality interactions in agroecosystems. J. Soil Water Conserv. 53: 224-229.

Richardson, A. E., and R.J. Simpson. 2011. Soil microorganisms mediating phosphorus availability. Plant Physiol. 156(3): 989-996.

Robles, Á., D. Aguado, R. Barat, L. Borrás, A. Bouzas, J.B. Giménez, N. Martí, J. Ribes, M.V. Ruano, J. Serralta, J. Ferrer, and A. Seco. 2020. New frontiers from removal to recycling of nitrogen and phosphorus from wastewater in the Circular Economy. Bioresour. Technol. 300: 122673–122673.

Rothe, M., A. Kleeberg, and M. Hupfer. 2016. The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments. Earth Sci Rev. 158: 51–64. https://doi.org/10.1016/j.earscirev.2016.04.008

Roychand, R., B. Kumar Pramanik, G. Zhang, and S. Setunge. 2020. Recycling steel slag from municipal wastewater treatment plants into concrete applications – A step towards

circular economy. Resour Conserv Recycl. 152: 104533. https://doi.org/10.1016/j.resconrec.2019.104533

Ruffatti, M. D., R.T. Roth., C.G. Lacey, and S.D. Armstrong. 2019. Impacts of nitrogen application timing and cover crop inclusion on subsurface drainage water quality. Agric. Water Manag. 211: 84–88.

Ruttenberg, K. C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Geochim. Cosmochim. Acta. 37: 1460−1482.

Sanchez, P.A., and G. Uehara. 1980. Management considerations for acid soils with high phosphorus fixation capacity. In F.E. Khasawneh, E.C. Sample, and E. J. Kamprath (eds.) The Role of Phosphorus in agriculture. SSSA, Madison, WI.

Sato, S., D. Solomon, C. Hyland, Q.M. Ketterings and J. Lehmann. 2005. Phosphorus speciation in manure and manure-amended soils using XANES spectroscopy. Environ. Sci. Technol. 39: 7485-7491.

Sengupta, S. and A. Pandit. 2011. Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer. Water Res. 45: 3318-3330.

Sengupta, S., T. Nawaz, and J. Beaudry. 2015. Nitrogen and Phosphorus Recovery from Wastewater Curr. Pollut. Rep. 1(3): 155–166. https://doi.org/10.1007/s40726-015-0013-1

Sharma, A., and D. Hesterberg. 2020. Synchrotron radiation-based spatial methods in environmental biogeochemistry. Editor(s): Regina M.B.O. Duarte, Armando C. Duarte, Multidimensional Analytical Techniques in Environmental Research. Elsevier. 231-265. https://doi.org/10.1016/B978-0-12-818896-5.00009-0.

Sharpley, A. N. 2003. Soil mixing to decrease surface stratification of phosphorus in manured soils. J. Environ. Qual. 35: 1375-1384.

Sharpley, A. N., and S. J. Smith. 1991. Effects of cover crops on surface water quality. In W. L. Hargrove (Ed.), Cover crops for clean water. Soil and Water Conservation Society, Ankeny, IA. 41-49.

Sharpley, A., and H. Tunney. 2000. Phosphorus research strategies to meet agricultural and environmental challenges of the 21st Century. J. Environ. Qual. 29: 176- 181.

Sharpley, A.N., L. Bergström, H. Aronsson, M. Bechmann, C.H. Bolster, K. Börling, F. Djodjic, H.P. Jarvie, O.F. Schoumans, C. Stamm, and K.S. Tonderski. 2015. Future agriculture with minimized phosphorus losses to waters: Research needs and direction. Ambio. 44: 163-179.

Shigaki, F., A. Sharpley, and L.I. Prochnow. 2007. Rainfall intensity and phosphorus source effects on phosphorus transport in surface runoff from soil trays. Sci. Total Environ. 373: 334-343.

Shigaki, F., and A. Sharpley. 2011. Phosphorus sources and soil properties effects on phosphorus availability. Soil Sci. 176(9).

Simeone, G. D. R., M. Muller, C. Felgentreu, and B. Glaser. 2020. Soil microbial biomass and community composition as affected by cover crop diversity in a short-term field experiment on a podzolized Stagnosol Cambisol. J. Plant. Nutr. Soil Sci. 183: 539-549.

Sims, J.T. and P.J.A. Kleinman. 2005. Managing agricultural phosphorus for environmental protection. In: J.T. Simms and A.N. Sharpley, editors, Phosphorus: Agriculture and the environment. ASA-CSSA-SSSA, Madison, WI. 1021-1068.

Sims, J.T., A.C. Edwards, O.F. Schoumans, and R.R. Simard. 2000. Integrating soil phosphorus testing into environmentally based agricultural management practices. J. Environ. Qual. 29: 60-71.

Smith, A. L., S.J. Skerlos, and L. Raskin. 2013. Psychrophilic anaerobic membrane bioreactor treatment of domestic wastewater. Water Res. 47(4): 1655–1665.

Smith, D. R., C. Huang, and R.L. Haney. 2017. Phosphorus fertilization, soil stratification, and potential water quality impacts. J Soil Water Conserv. 72(5): 417-424.

Smith, D. R., S.J. Francesconi, S.J. Livingston, and C. Huang. 2015. Phosphorus losses from monitored fields with conservation practices in the Lake Erie Basin, USA. Ambio, 44 (2): S319-S331.

Smith, S.J., A.N. Sharpley, J.W. Nancy, W.A. Berg, and O.R. Jones. 1991. Water quality impacts associated with wheat culture in the southern plains. J. Environ. Qual. 20: 244-249.

Sposito, G. 1989. The Chemistry of Soils. xiii 277 pp. New York, Oxford: Oxford University Press. ISBN 0 19 504615 3.

Srivastava, P., S. Rishikesh, T. Sachchidanand, and S.R. Akhilesh. 2016. An urgent need for sustainable thinking in agriculture – an Indian scenario. Ecol. Indic. 67: 611- 622.

Starr, L.M. 2021. Linkages between cover crops, phosphorus fertilizer management, soil health, and phosphorus bioavailability in replicated research watersheds. Doctoral Dissertation, Kansas State University. K-State Research Exchange.

Stratful, I., M.D. Scrimshaw, and J.N. Lester. 2001. Conditions influencing the precipitation of magnesium ammonium phosphate. Water Res. 35: 4191–4199.

Susan, S. 2011. Geochemical instrumentation and analysis. Scanning Electron Microscope. University of Wyoming. https://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html

Syers, J.K., A.E. Johnston, and D. Curtin. 2008. Efficiency of soil and fertilizer phosphorus use: Reconciling changing concepts of soil phosphorus behavior with agronomic information. FAO Fertilizer and Plant Nutrition Bulletin 18.

Szogi, A.A., P.J. Bauer, and M.B. Vanotti. 2012. Vertical distribution of phosphorus in a sandy soil fertilized with recovered manure phosphates. J. Soil Sediments. 12: 334-340.

Talboys, P.J., J. Heppell, T. Roose, J.R. Healey, D.L. Jones, and P.J.A. Withers. 2016. Struvite: a slow-release fertilizer for sustainable phosphorus management. Plant Soil. 401: 109-123.

Tchobanoglous, G., H.D. Stensel, R. Tsuchihashi, F.L. Burton, M. Abu-Orf, G. Bowden, W. Pfrang. 2014. Wastewater Engineering: Treatment and Resource Recovery. 5th edition. McGraw Hill, New York, N.Y.

Teboh, J. M., and D.W. Franzen. 2011. Buckwheat (Fagopyrum esculentum Moench) potential to contribute solubilized soil phosphorus to subsequent crops. Commun Soil Sci Plant Anal. 42(13): 1544-1550.

TerAvest, D., L. Carpenter-Boggs, C. Thierfelder, and J.P. Reganold. 2015. Crop production and soil water management in conservation agriculture, no-till, and conventional tillage systems in Malawi. Agric. Ecosyst. Environ. 212: 285–296.

Tervahauta, T., R.D. van der Weijden, R.L. Flemming, L. Hernández Leal, G. Zeeman, and C.J. Buisman. 2014. Calcium phosphate granulation in anaerobic treatment of black water: A new approach to phosphorus recovery. Water Res. 48(1): 632–642. https://doi.org/10.1016/j.watres.2013.10.012

Tiessen, H., J. W B. Stewart, and C. V. Cole. 1984. Pathways of phosphorus transformations in soils of differing pedogenesis. Soil Sci. Soc. Am. J. 48: 853–858.

Tiessen, H., P. Chacon and E. Cuevas. 1994. Phosphorus and nitrogen status in soils and vegetation along a toposequence of dystrophic rain-forests on the upper rio-negro. Oecologia. 99: 145-150.

Toor, G. S., S. Hunger, J.D. Peak, J. T. Sims, and D. L. Sparks. 2006. Advances in the characterization and of phosphorus in organic wastes: environmental and agronomic applications. Advan. Agron. 89: 1–72.

Toor, G.S., J.D. Peak and J.T. Sims. 2005. Phosphorus speciation in broiler litter and turkey manure produced from modiried diets. J. Environ. Qual. 34: 687-697.

Tran, A. T. K., Y. Zhang, D. De Corte, J.B. Hannes, W. Ye, P. Mondal, N. Jullok, B. Meesschaert, L. Pinoy, and B. Van der Bruggen. 2014. P-recovery as calcium phosphate from wastewater using an integrated selectrodialysis/crystallization process. J. Clean. Prod. 77: 140–151. https://doi.org/10.1016/j.jclepro.2014.01.069

Turner, B. L., I.D. McKelvie, and P.M. Haygarth. 2002. Characterization of water-extractable soil organic phosphorus by phosphatase hydrolysis. Soil Biol. Biochem. 34: 27-35.

United States Department of Agriculture, Economic Research Service. ERS annual report, 2017.

Vadas, P.A, L.B. Owens, and A.N. Sharpley. 2008. An empirical model for dissolved phosphorus in runoff from surface-applied fertilizer. Agric. Ecosyst. Eniron. 127: 59-65.

Vadas, P.A., W.E. Jokela, D.H. Franklin, and D.M. Endale. 2011. The effect of rain and runoff when assessing timing of manure application and dissolved phosphorus loss in runoff. J. Am. Water. Resour. Assoc. 47: 877-886.

Vandamme, E., M. Renkens, P. Pypers, E. Smolders, B. Vanlauwe, and R. Merckx. 2013. Root hairs explain P uptake efficiency of soybean genotypes grown in a P-deficient Ferralsol. Plant Soil. 369: 269-282.

Veneklaas, E.J., H. Lambers, J. Bragg, P.M. Finnegan, C.E. Lovelock, W.C. Plaxton, C.A. Price, W.R. Scheible, M.W. Shane, P.J. White and J.A. Raven. 2012. Opportunities for improving phosphorus-use efficiency in crop plants. New Phytol. 195: 306-320. https://doi.org/10.1111/j.1469-8137.2012.04190.x

Wang, S., J. Xiangcan, Z. Haichao, Z. Xiaoning, and F. Wu. 2007. Effect of Organic Matter on the Sorption of Dissolved Organic and Inorganic Phosphorus in Lake Sediments. Colloid Surf. A-Physicochem. Eng. Asp. 297: 154-162. https://doi.org/10.1016/j.colsurfa.2006.10.040.

Weeks, J.J., and G.M. Hettiarachchi. 2020. Source and formulation matter: new insights into phosphorus fertilizer fate and transport in mildly calcareous soils. Soil Sci. Soc. Am. J. 84: 731–746.

Weins, J.T., B.J. Cade-Menun, B. Weiseth, and J.J. Shoenau. 2019. Potential phosphorus export in snowmelt as influenced by fertilizer placement method in the Canadian prairies. J. Environ. Qual. 48: 586–593.

White, G.N. 2008. Scanning electron microscopy.p 269-297. In Ulery and Dress (ed.) Methods of soil analysis. Part. 5. SSSA, Madison, WI.

White, P.J., and J.P. Hammond eds. 2008. The ecophysiology of plant–phosphorus interactions. Dordrecht, the Netherlands: Springer.

Wilfert, P., A.I. Dugulan, K. Goubitz, L. Korving, G.J. Witkamp, and M.C.M. Van Loosdrecht. 2018. Vivianite as the main phosphate mineral in digested sewage sludge and its role for phosphate recovery. Water Res. 144: 312–321. https://doi.org/10.1016/j.watres.2018.07.020

Wu, H., A. Ikeda-Ohno, Y. Wang, and T.D. Waite. 2015. Iron and phosphorus speciation in Fe-conditioned membrane bioreactor activated sludge. Water Res. 76: 213–226. https://doi.org/10.1016/j.watres.2015.02.020

Wu, Y., J. Luo, Q. Zhang, M. Aleem, F. Fang, Z. Xue, and J. Cao. 2019. Potentials and challenges of phosphorus recovery as vivianite from wastewater: A review. Chemosphere. 226: 246–258. https://doi.org/10.1016/j.chemosphere.2019.03.138

Yang, S., and J. Bae. 2014. A feasibility of coagulation as post-treatment of the anaerobic fluidized bed reactor (AFBR) treating domestic wastewater. J. Korean Soc. Water Qual. 28(6): 623–634. https://doi.org/10.11001/jksww.2014.28.6.623

Yuan, M., F. G. Fernández, C. M. Pittelkow, K. D. Greer, and D. Schaefer. 2018. Tillage and fertilizer management Eefects on phosphorus runoff from minimal slope fields. J. Environ. Qual. 47(3): 462.

Zare, M., A.A. Samani Nazari, M. Mohammady, T. Teimurian, and J. Brazrafshan. 2016. Simulations of soil erosion under the influence of climate change scenarios. Environ. Earth Sci. 75: 1405.

Zeimen, M.B., K.A. Janssen, D.W. Sweeney, G.M. Pierzynski, K.R. Mankin, D.L. Devlin, D.L. Regehr, M.R. Langemeier, and K.A. Mcvay. 2006. Combining management practices to reduce sediment, nutrients, and herbicides in runoff. J. Soil Water Conserv. 61: 258-267.

Zhang, T., L. Ding, H. Ren, Z. Guo, and J. Tan. 2010. Thermodynamic modeling of ferric phosphate precipitation for phosphorus removal and recovery from wastewater. J. Hazard. Mater. 176(1): 444–450. https://doi.org/10.1016/j.jhazmat.2009.11.049

Zheng, X., Y. Ye, Z. Jiang, Z. Ying, S. Ji, W. Chen, B. Wang, and B. Dou. 2020. Enhanced transformation of phosphorus (P) in sewage sludge to hydroxyapatite via hydrothermal carbonization and calcium-based additive. Sci. Total Environ. 738: 139786. https://doi.org/10.1016/j.scitotenv.2020.139786

Zhou, Q., S. Daryanto, Z. Xin, Z. Liu, M. Liu, X. Cui, and L. Wang. 2017. Soil phosphorus budget in global grasslands and implications for management. J. Arid Environ. 144: 224-235.

Chapter 3 - Recovered iron- based phosphorus products from municipal wastewater: Fate and behavior in a selected calcareous soil

Abstract

The demand for P sources is increasing with the growing world population, raising the need for exploring safe and efficient secondary P fertilizer sources. Wastewater is a renewable resource and recovered nutrient products (RNPs) from wastewater may contain high concentrations of plant-available nutrients and thus, can be promising alternative fertilizers. This study evaluated the effectiveness of Fe- based RNP, recovered from Fort Riley, Kansas municipal wastewater, using an innovative anaerobic membrane bioreactor (AnMBR) technology. The overall aims of the study were to characterize the Fe- based RNP and evaluate the dissolution, transformations, and potential bioavailability of P in Fe- based RNP compared to conventional P fertilizers in alkaline mildly calcareous using short-term laboratory incubation studies. Soils were incubated for 1-day, 3-days, 1-week, 2-weeks and 5-weeks in Petri dishes with four treatments: Fe- based RNP, monoammonium phosphate (MAP), and triple superphosphate (TSP) plus control. After each period, soils were sectioned at different distances from the point of application and soil pH, total P (to assess the P diffusion) and resin extractable P (to assess potential plant availability) were measured. Phosphorus diffused from the center section to the next section in all treatments. Percent resin extractable P also increased during the study period. The Fe- based RNPs showed a lower solubility and extractability than the conventional fertilizers compared. Iron-based P-rich RNPs may not be an effective fertilizer product, as they can act as a P sink in some agricultural systems instead of a source.

Introduction

Phosphorus (P) is a vital, geographically concentrated, nonrenewable resource necessary to support global food production (Mayer et al., 2016). Soils may have different pools of P, but plant uptake is limited to a small soluble fraction (Smil, 2000; Sohrt et al., 2017) due to complex processes and interactions with soil components such as calcium in alkaline soils and iron and aluminum hydroxides in acidic soils (Lindsay, 1979; Bindraban et al., 2020). Farmers and growers must consider this when fertilizing their crops to ensure optimal plant growth and health. Nonrenewable phosphate rock with finite reserves, which are only in limited locations worldwide, is the current primary source of P (Walan et al., 2014; Schroder et al., 2010). Modern agriculture heavily depends on massive inputs of fertilizers, including P, which is mined at a global rate of around 20 million metric tons per year (Cordell et al., 2011). Thus, economically extractable rock phosphate will eventually become scarce as it is exploited at higher rates. While it has been proven to increase yield, overloading soils with nutrients can have negative environmental impacts such as eutrophication, hypoxic zones, and harmful algal blooms in surface waters. As we move forward, sustainable management of nutrients in agricultural systems has become a grand challenge for the 21st century (Zhang et al., 2020). Several concerns have been raised due to the rapid and increasing P consumption in modern agriculture on both its supply security (Godfray et al., 2010; Scholz & Wellmer, 2013) and its environmental impact (Sharpley & Tunney, 2000; Ranatunga et al., 2013). It is uncertain how long these reserves will be available, but experts predict that demand may surpass supply within our lifetime, potentially as soon as 2035 (Cordell et al., 2011; Cordell & White, 2013; Mayer et al., 2016). The proper utilization of soil P and P-containing mineral and organic fertilizers, along with the cradle-to-cradle recycling of P from municipal, agricultural, and other biodegradable waste sources as

green renewable fertilizers with high P use efficiency (e.g., slow-release granules), has become increasingly vital (Ma et al., 2011; Schroder et al., 2011; Huang et al., 2012; Zhang et al., 2013).

Considering wastewater as part of the circular economy is becoming increasingly important (Robles et al., 2020; Roychand et al., 2020). The potential benefits of wastewater are that it contains valuable nutrients such as P and nitrogen (N) that can be used for fertilizer production. Additionally, wastewater can be treated and reused as water, and its organic matter can be harnessed for energy production (Robles et al., 2020). Recent studies have shown that using agricultural waste for food production applications has made significant progress (Sonmez et al., 2016; Turan et al., 2019; Klammsteiner et al., 2020). Biological nutrient removal (BNR) systems have been developed to remove N and P together from municipal wastewater and produce a clean effluent that meets stringent total N and P discharge regulations (Bashar et al., 2018). However, beneficial recovery of these valuable nutrients has limited success in BNR systems, as the N is transformed to nitrogen gas and P remains trapped in the settled BNR sludge, with biosolids land application being the dominant reuse option (Tchobanoglous et al., 2014). Apart from removal, several options are available for a more effective P recovery from municipal or agricultural wastewater. Other widely explored methods include chemical coagulation, flocculation processes, and bioelectrochemical systems, membrane-based, and photosynthetic-based processes (Robles et al., 2020).

Anaerobic membrane bioreactors (AnMBRs) have been gaining attention as an innovative environmental biotechnology solution that has the potential to not only treat concentrated wastewater but also recover water, energy, and nutrients (Liao et al., 2006; Lin et al., 2013). The AnMBRs offer a promising sustainable resource recovery and waste management platform by combining membrane filtration techniques and anaerobic biological treatment (Lim

et al., 2019). This technique converts high-strength wastewater to high-effluent standards with a reduced footprint (Lim et al., 2019). The AnMBR can produce methane from anaerobic processes, and a high-quality effluent containing N and P in the liquid phase could be used for fertigation (Robles et al., 2020). Wastewater treatment plants add iron via ferric chloride to control odor from hydrogen sulfide formation (Gutierrez et al., 2010). In municipal wastewater in anaerobic systems, mineral vivianite is known to precipitate when residual ferrous iron is present, emerging as an alternative for P recovery (Rothe et al., 2016; Wilfert et al., 2018). Although Wilfert et al., 2018 were able to detect and quantify vivianite in municipal digested sludge, its effectiveness in the soil as a P fertilizer product for plant uptake was not assessed. When wastewater is dosed with iron other than vivianite, various amorphous iron phosphate minerals and iron hydroxide minerals are also known to precipitate (Wu et al., 2015).

The pilot scale gas sparged AnMBR (1000 gal/day capacity) that was successfully operated at Fort Riley, Kansas, for over 18 months also investigated the recovered nutrient products (RNPs) from the permeate using a coagulation-flocculation-sedimentation (CFS) unit (Lim et al., 2019). The nutrient contents in the RNPs may vary with the wastewater composition, characteristics, and the treatment technologies applied. In addition to iron and phosphate, these iron-based P-rich RNPs may contain high concentrations of other metals and anionic ligands, affecting phosphorus release and availability to plants (Heronemus et al., 2021). Understanding the potential availability of nutrients when these RNPs are used as a soil amendment or fertilizer is essential to characterize these RNPs. In P recovery studies, many techniques such as X-ray diffraction (XRD) (Ippolito et al., 2003; Massey et al., 2010; Zohar et al., 2018), scanning electron microscopy (SEM) examination coupled with energy dispersive X-ray spectroscopy (EDX) (Massey et al., 2010; Zohar et al., 2018; Battistoni et al., 2001), and X-ray absorption

near-edge structure spectroscopy (XANES) (Massey et al., 2018; Massey, 2019) have been used. Soil incubation studies can be used to evaluate nutrient release, diffusion, and potential plant availability (Lombi et al., 2004; Hettiarachchi et al., 2008; Pierzynski & Hettiarachchi, 2018; Weeks & Hettiarachchi, 2020; Heronemus et al., 2021). Minimal data are available regarding the potential use of these RNPs in soils. Therefore, the overall aims of this study were to characterize and compare the Fe-based P rich RNPs recovered from municipal wastewater using an innovative AnMBR technology. Dissolution, transformations, and potential bioavailability of P in the Fe-based P rich RNPs were investigated with conventional P fertilizers in a selected calcareous soil using short-term laboratory incubation studies combined with wet chemical and synchrotron-based x-ray techniques.

Materials and Methods

Recovered nutrient product recovery

Several bench scale jar testings were initially conducted in the laboratory using the method described in Section 2.1 in Heronemus et al., 2021. An actual permeate from the AnMBR with a cationic polymer (to ensure adequate settle ability for a wastewater-derived product) was used in the pilot scale AnMBR site. The continuous pilot scale CFS unit was operated at a cationic polymer at 1 mg/L and 110mg/L of ferric chloride and aluminum chlorohydrate concentrations as Fe, 30mg/L as Al (Heronemus et al., 2021). At different stages of the treatment process, P and sulfide levels, residual sulfide, and total P were measured using the methods described in Section 2.3 in Heronemus et al., 2021. The original RNP sample was collected during the steady-state operation of the pilot scale AnMBR CFS unit.

Product characterization

A semi-solid nutrient-rich sample was freeze-dried and digested using the USEPA method SW846-3051A (USEPA, 2007) in a microwave digestion unit. The digestate was analyzed for the nutrient composition and the selected potentially toxic trace elements using an inductively coupled plasma optical emission spectrometer or ICP-OES (720-ES, Varian, Santa Clara, CA) and an inductively coupled plasma mass spectrometer or ICP-MS (7500cx, Agilent, Santa Clara, CA). The freeze-dried product was directly used for the powder XRD analysis to identify existing nutrient phases in the RNP using PANalytical Empyrean Multi-Purpose X-Ray Diffractometer (Spectris Company, Egham, Surrey, UK) using Cu Kα radiation at a wavelength of 1.54 Å and generator settings of 45 kV and 40 mA. Measurements were made using a continuous scanning technique from 5 to 70 °2θ and a scan speed of 0.024° per second. The SEM-EDX spectroscopy analysis was also performed using a Hitachi S-3500 N scanning electron microscope equipped with a Model S-6542 absorbed electron detector (Hitachi Science Systems, Ibaraki, Japan) at an accelerating potential of 5 kV. Further product characterization was done using XANES spectroscopy at Sector 9-BM-B, Advanced Photon Source, Argonne National Laboratory, Argonne, IL. Detailed methods are described in Section 2.4.1 in Heronemus et al., 2021.

Transformations, reaction pathways, and availability of RNP in soils

A short-term laboratory incubation study was conducted using alkaline, mildly calcareous silt loam soil from Garden City, Kansas. This soil was selected due to the limited solubility of iron phosphate. In alkaline soils, theoretically, can expect higher solubility than in acid soils (Lindsay, 1979). The soil was collected at a depth of 10 cm, air-dried, and sieved to <2mm before the experiments. The pH, available P, cation exchange capacity (CEC), carbonate content,

total P, maximum water holding capacity (MWHC), total organic C, and soil texture were determined using the methods described in Section 2.4.2 in Heronemus et al., 2021.

Section 2.4.2 in Heronemus et al., 2021 describes the detailed incubation study setup. Briefly, the setup is as follows. Petri dishes were packed with a pre-moist soil to a bulk density of 1.0 gcm^{-3} and then added the remaining moisture to achieve 55% of the soil's maximum water-holding capacity. They were left to equilibrate for 24 h at room temperature, and the powdered treatments were placed in the center of the dish, just below the soil surface, and covered with soil. The treatments were control, mono ammonium phosphate (MAP), triple superphosphate (TSP), and Fe- based RNP with four replicates per each treatment. After adding the treatments, Petri dishes were closed and wrapped again with Parafilm (Bemis Flexible Packaging, Neenah, WI) wrapped in aluminum foil, and incubated (Precision Low Temp Incubator, Waltham, MA) in the dark at 25 °C. The study was conducted for five incubation periods of 1-day, 3-days, 1-week, 2-weeks and 5-weeks. Plates were opened at the end of each period, and the soils were collected from 0 to 7.5, 7.5 to 13.5, 13.5 to 25, and 25 to 43.5mm from the point of application as concentric rings.

Soil pH, total P and resin extractable P were determined using the methods described Heronemus et al., 2021 for all samples. Total P (determined using aqua regia digestion (without H_2O_2 pretreatment) and analyzed via ICP-OES) data were normalized by calculating the percentage of P added (PPA) for each dish section for all treatments (Hettiarachchi et al., 2010) is defined as follows:

$$PPA = \frac{(P_f)S_i \times M_i}{\sum_{i=1-4}[(P_f)S_i \times M_i]} \times 100$$

where i is the dish section (1–4), $(P_f)S_i$ is the concentration of P fertilizer in each dish section, and M_i is the mass of soil in each dish section. The $(P_f)S_i$ is calculated by subtracting the total P concentration of the unfertilized soil sample from the total P concentration in the fertilized dish section.

Resin P was determined by the anion exchange resin (AER) technique (Myers et al., 2005) and quantified colorimetrically using a Beckman-Coulter DU-800 spectrophotometer (Brea, CA) (Murphy & Riley, 1962). The percentage of resin extractable P (PRP) for each dish section for all treatments were calculated according to the following equation (Pierzynski & Hettiarachchi, 2018):

$$PRP = \frac{REP_i}{Total\ P_i} \times 100$$

where i is the dish section (1–4), REP_i is the resin P concentration, and $Total\ P_i$ is the total P concentration in the i^{th} dish section.

Statistical analysis

Proc MIXED procedure in SAS (SAS Institute, 2011) was used to analyze all soil data. The experimental design was a complete randomized design. Data were analyzed via ANOVA with P fertilizer treatment as the main treatment and dish sections as subplot treatments. The Tukey's HSD test was used to compare all treatments at an p = 0 .05 significance level.

Results and Discussion

Characterization of the recovered nutrient product

The recovered product contained 2.58% of P along with significant amounts of Fe, Al, and S, accounting for approximately 20%, 19%, and 15% of the total composition of RNP, respectively (Table 3.1). Significant amounts of Al and Fe in this RNP were primarily from the iron and aluminum salts used for P precipitation in the CFS unit (Heronemus et al., 2021).

Municipal wastes and animal manures generally have lower total and water-soluble P concentrations than mineral P fertilizers and contain varying amounts of organic P and other elements that may affect P availability to plants (Hedley & McLaughlin, 2005). The measured trace element concentrations were low (Table 3.1). Recovered products from waste streams cause the potential presence of heavy metals (i.e., metallic elements heavier than that of Fe), organic micropollutants, and pathogens, which raises concerns (Cunha et al., 2020). Therefore, each country has established regulations and demands for fertilizer quality, efficiency, and composition (Breckenridge & Crockett, 1998). According to these regulations, the quality of fertilizers is understood as the maximum allowed concentration of contaminants and desired P content and its plant availability.

Table 3.1. Selected major and trace elemental composition of the recovered nutrient product.

Major Element †	Concentration % (w/w)	Trace Element ‡	Concentration (mg/kg)
P	2.58±0.04	**Cr**	34.27±2.01
Fe	20.17±0.38	**Cu**	33.55±1.73
Al	19.29±0.17	**Zn**	16.82±0.38
S	15.03±0.18	**As**	9.01±1.18
Ca	0.42±0.00	**Mo**	7.17±0.03
Na	0.18±0.00	**B**	4.15±0.85
K	0.09±0.00	**Pb**	2.06±0.05
Mg	0.07±0.01	**Cd**	0.04±0.00

†Measured using inductively coupled plasma optical emission spectrometer (ICP-OES)
‡Measured using inductively coupled plasma mass spectrometer (ICP-MS)

A powder XRD analysis was done to identify existing nutrient phases in the Fe-based P-rich RNP. Due to its amorphous nature and lack of crystallinity, there were no identifiable

diffraction lines with an enhanced background signal for the RNP (Figure 3.1). The XRD technique provides insights into crystalline structures, and its detection limit is about 2 wt.% of the sample (Klug & Alexander. 1974; Ali et al., 2022). The conditions of formation of the recovered products result in physical and chemical differences in the products (Massey et al., 2010). According to Stratful et al., 2001, retention time is associated with the size of recovered crystals, where crystal size is increased with increased retention time. In complex wastewater matrices, organic matter or other ions could interfere with crystallization by blocking crystal growth sites and delaying crystal formation (Massey et al., 2010). Heronemus et al., 2021 also observed different XRD patterns for the same RNP but from a different batch where one had prominent calcite ($CaCO_3$) peaks and lower peak intensities for iron phosphates and aluminum oxides and other no identifiable peaks.

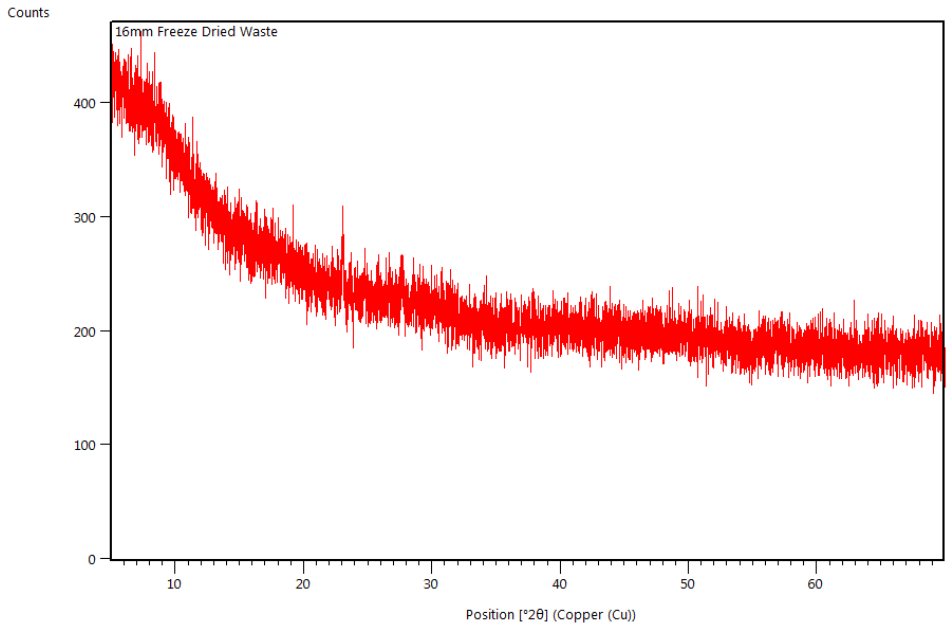
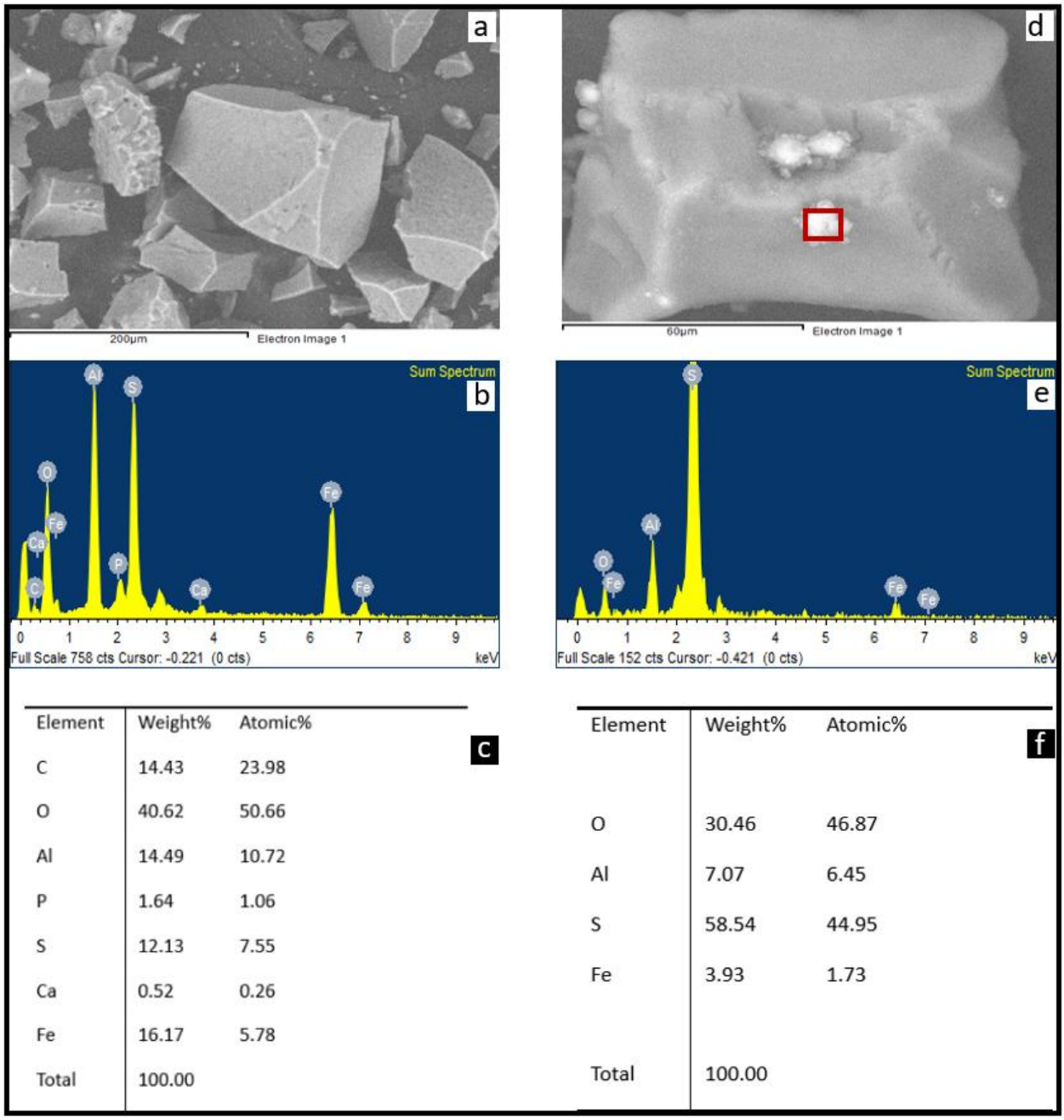


Figure 3.1. The X-ray diffractogram of the recovered nutrient product

Further characterization of RNP was done using SEM-EDX. Figure 3.2a showed that the particles were small, irregular, and homogeneous. The data collected from backscattered electron (BSE) images-EDX showed that the product was rich in Fe, Al and S (Figure 3.2b, 3.2c). The selected bright-colored spot showed that it was rich in S (Figure 3.2d, 3.2e, 3.2f), which could be elemental S. The atomic number sensitivity of BSE images can be used to differentiate particles with varying chemical compositions. Moreover, EDX can be used to determine the elemental composition on the surface. Regions displaying a high average atomic number will appear brighter than those with a low one. The results confirmed the presence of high Fe, Al, and S in the product obtained from the total elemental composition. The information from SEM-EDX analysis is used to identify the crystal structure and the structural information of waste-derived products (Massey et al., 2010). Bowers et al., 2007 showed Mg phosphate crystals precipitated on the struvite's Ca phosphate seed material surface. Massey et al., 2010 also used SEM–EDX analysis to differentiate the chemical and physical differences in the recovered materials obtained from dairy and food processing wastewater.



c

Element	Weight%	Atomic%
C	14.43	23.98
O	40.62	50.66
Al	14.49	10.72
P	1.64	1.06
S	12.13	7.55
Ca	0.52	0.26
Fe	16.17	5.78
Total	100.00	

f

Element	Weight%	Atomic%
O	30.46	46.87
Al	7.07	6.45
S	58.54	44.95
Fe	3.93	1.73
Total	100.00	

Figure 3.2. (a) Backscattered electron (BSE) image of the recovered nutrient product (RNP). (b) Elemental composition of (a) by energy dispersive X-ray (EDX) spectroscopy. (c) Table of elemental composition of (b). (d) The BSE image of a zoomed particle in the RNP sample. Area where the elemental analysis was conducted is outlined in pink. (e) Elemental composition of the selected area shown on (d) by EDX. (f) Table of elemental composition of (d).

X-ray absorption near-edge structure spectroscopy analysis of the RNP sample was given by Heronemus et al., 2021. The XANES spectra analysis showed that this product was rich in iron adsorbed-P, especially goethite sorbed-P and vivianite-like P. The absence of pre-edge implies that these P solids do not possess a well-defined crystalline structure, and the residual (minor un-fitted parts) might result from the product's heterogeneous nature. The XANES result supported the XRD analysis. Massey, 2018 also used bulk P K-edge XANES to obtain a quantitative estimation of the relative struvite and apatite proportions in the crystalline and sandy struvite materials. Zohar et al., 2018, and Massey et al., 2018 used combined chemical extractions, SEM-EDX, and XANES spectroscopy to quantify speciation in P recovered from wastewater.

The purity, size, and morphology of recovered materials as critical factors in the materials' successful recovery and re-use as fertilizer (Le Corre et al., 2007). More importantly, material differences could affect their fertilizer effectiveness. Babic-Ivancic et al., 2002 found that chemically identical, different struvite morphologies, including dendritic and rod-like crystals, have different dissolution kinetics linked to differences in surface area. Chemical differences in the recovered products may also affect solubility and P availability over time as the materials dissolve in soil solution. Recovered P availability and uptake of P by crops depend greatly on soil conditions, the type of P fertilizer applied, and specific crop characteristics (Massey et al., 2019; Vogel et al., 2017).

Potential plant availability of RNP in soils

Selected physical and chemical properties of the soil used for the incubation study, showed characteristics of a mildly calcareous soil with 5.6% $CaCO_3$ (Table 3.2).

Table 3.2. Selected physical and chemical properties of the soil used for the incubation study.

Parameter	Value
pH (1:10 soil:water)	8.8±0.1
EC, mS/cm	1.3
CEC, $cmol_c/kg$	18.3
TOC, %	1.1
$CaCO_3$, %	5.6
Total N, %	0.17
Total P, mg/kg	634±1
Available P, mg/kg	61.5
Texture	Silt Loam
(Sand, Silt, and Clay, %)	(24.9, 52.4, 22.7)

Diffusion of P

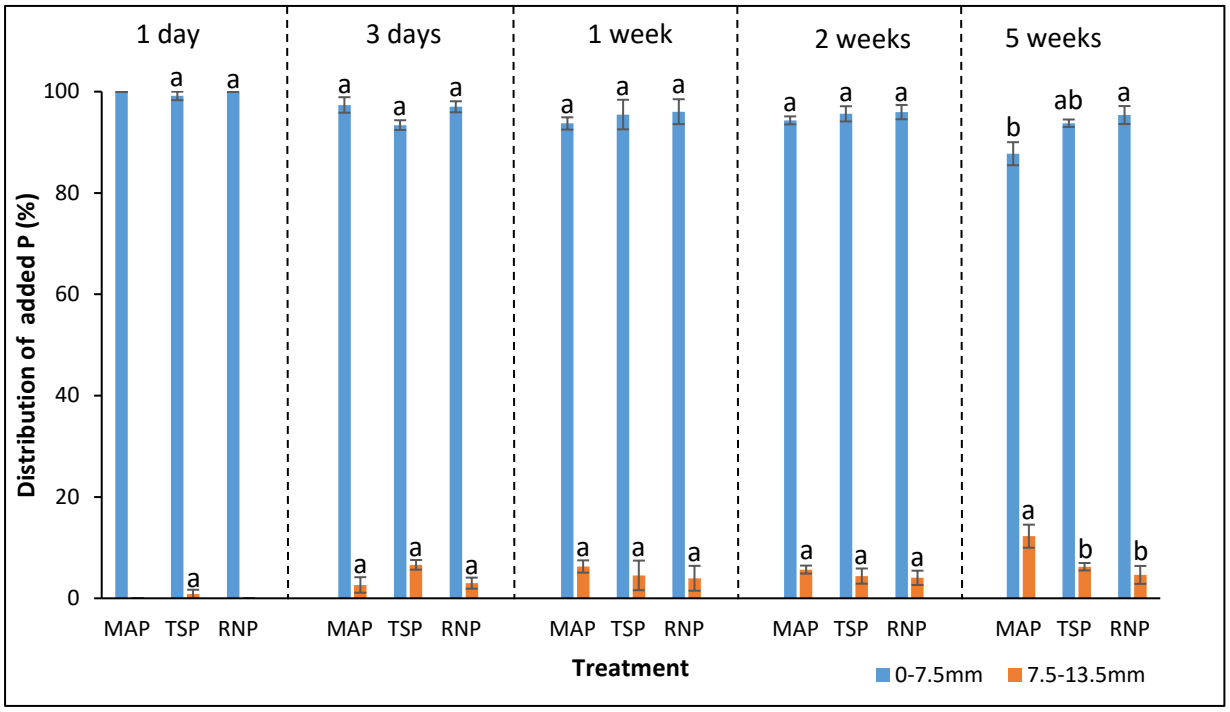


Figure 3.3. Distribution of added P (%) after 1day, 3 days, 1 week, 2 weeks and 5 weeks of incubation in calcareous soil. Means within a soil section for each treatment each time period containing the same letter are not significantly different at *p* = 0.05 according to Tukey's pairwise method.

The P diffusion in this mildly calcareous soil showed that most P added remained within the first section for all time durations (Figure 3.3). Phosphorus diffusion was greater for MAP, followed by similar amount of TSP, and RNP to the second section after 5 weeks. This could be attributed to the initial acidulation effect of TSP and MAP treatments (Figure 3.4). Soon after the addition (after 1 day) of treatments P diffusion was greater for TSP. However, P diffusion in all treatments from the center to the next section was same at the end of 3 days and the same trend continued till 2 weeks (Figure 3.3). The overall reduction in diffusivity observed with MAP and TSP treatments in this mildly calcareous soil may be a result of a combination of the impediment of P fertilizer movement outward by the silt loam texture and immediate formation of Ca-P precipitates upon addition of P fertilizer. In calcareous soils low P solubility, diffusion and crop

uptake is mainly due to fertilizer-soil reactions removing plant available P from the soil solution pool and forming poorly soluble P pools (Rafullah et al., 2020; Taalab et al., 2019). Several studies including Hettiarachchi et al., 2006, Lombi et al., 2004, Weeks & Hettiarachchi, 2020, have also documented that the limited movement of added nutrients in calcareous soils is due to the strong precipitation and sorption reactions that occur with calcium in the soil solution, solid calcium carbonates and other colloids/surface coatings. Higher clay and calcium carbonate contents would increase the number of P reactive sites per given soil volume and decrease average solution P concentrations. Slow diffusion could be due to the decreased solution concentration and reduced slope gradient. (Weeks & Hettiarachchi, 2020, Olsen & Watanabe, 1963). In this soil, after 5 weeks of incubation, diffusion of TSP was lower compared to MAP. The P species in TSP is monocalcium phosphate (MCP), which leads to direct acidification. However, the indirect acidification by MAP reduces the pH in the long term, which is favorable for more dissolution. This is further discussed in the next section. Similar results were observed for MAP and TSP diffusion in petri dish experiments in calcareous soils by Lombi et al., 2004.

Potential plant available P and pH

Plant uptake studies and different extraction procedures are used to determine plant availability of P. Even though soils contain different pools of P that could be several thousand times higher than required for plant growth, only a small soluble fraction is available for plant uptake (Smil, 2000; Sohrt et al., 2017). Labile P in soil appears to be isotopically exchangeable or anion resin extractable. Resin extractable P measures potential plant available P concentration in soils (Myers et al., 2005). The resin-extractable P method is superior to most common extraction procedures such as Olsen P, Bray 1-P, and Mehlich P for determining plant available P (Saggar et al., 1990).

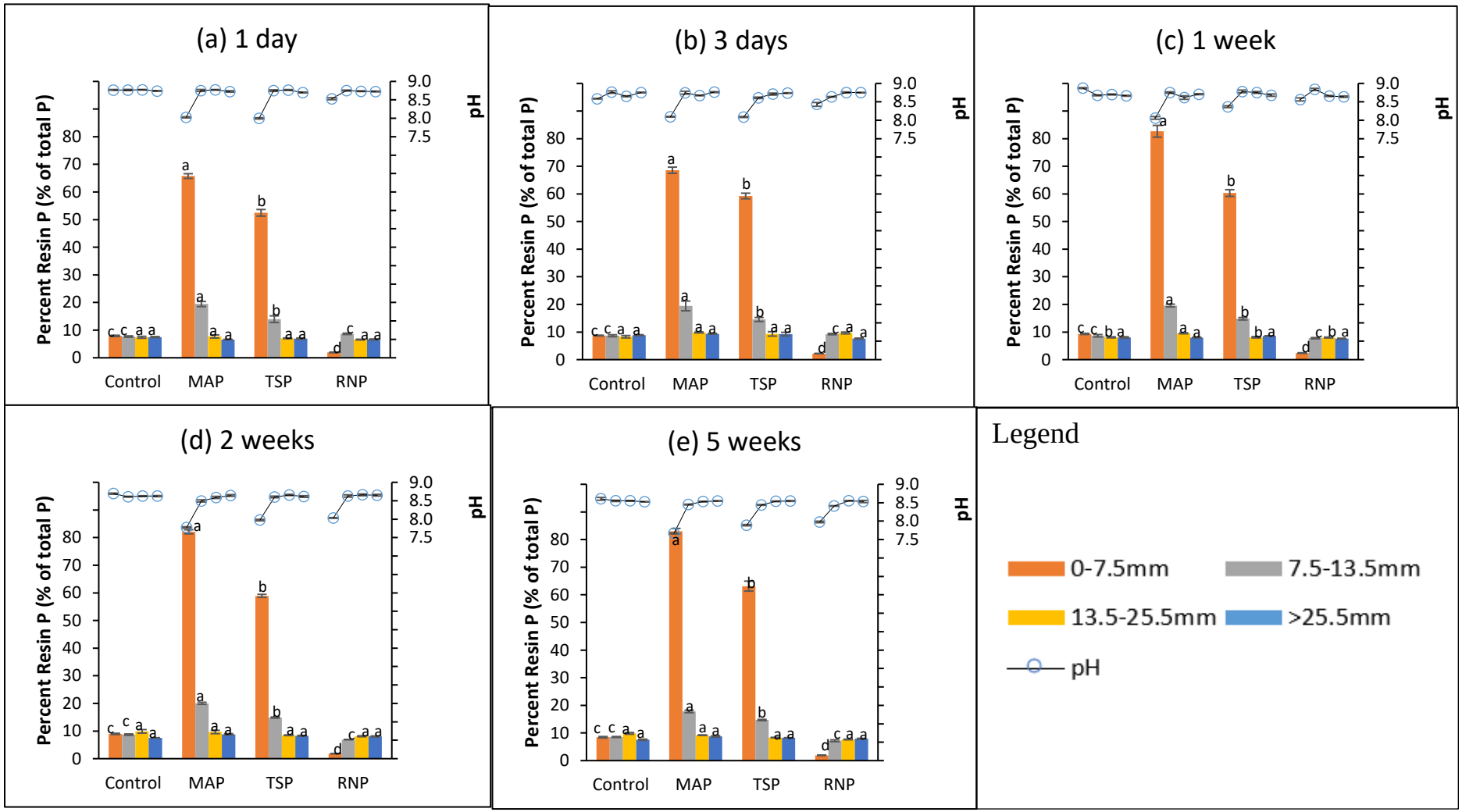

(a) 1 day
(b) 3 days
(c) 1 week
(d) 2 weeks
(e) 5 weeks
Percent Resin P (% of total P)
pH
Control
MAP
TSP
RNP
Legend
0-7.5mm
7.5-13.5mm
13.5-25.5mm
>25.5mm
pH

Figure 3.4. Percent resin P (PRP) and the pH for each dish section for all treatments after (a) 1 day, (b) 3 days (c) 1 week (d) 2 weeks and (c) 5 weeks of incubation in calcareous soil. Means within a soil section for each treatment containing the same letter are not significantly different at $p = 0.05$ according to Tukey's pairwise method.

In calcareous soil after 1 day of incubation, the highest availability of PRP was in the center section of MAP and TSP-added treatments, whereas the center section of RNP showed lowest PRP availability and it was even lower than the control. This trend continued through 5 weeks (Figure 3.4). However, with time, P availability in the center section and second section of MAP and TSP increased very slowly and showed the highest availability of PRP after 5 weeks (Figure 3.4). Though RNP amended treatment showed significantly lower PRP than the control for the center section, all other sections showed similar PRP as the control throughout the incubation time (Figure 3.4) and that is likely due to no appreciable movement of RNP-P in to other sections (Figure 3.3).The maximum pH reduction was observed in the center section of MAP and TSP and, as moving away from the center, pH became similar to the control soil pH in all time durations (Figure 3.4). As mentioned above, phosphate adsorption and precipitation reactions with calcium carbonate determine the P availability in calcareous soils. Different factors such as carbonate content, different Ca:P ratios, and pH at the moment of precipitation would impact the type of Ca-P that forms, mineral crystallinity, which determines the solubility (Baig et al., 1999; Raynaud et al., 2002; Wang & Nancollas, 2008; Lei et al., 2017; Weeks & Hettiarachchi, 2020).

The pH reduction of MAP compared to the control is due to the acidification caused by the nitrification process of the ammonium-N in the phosphorus fertilizers. (Hanson & Westfall, 1985). However, the overall buffering capacity of the soil carbonates limits this reaction (Lombi

et al., 2004; Hettiarachchi et al., 2010). This pH reduction causes more PRP in the center section in MAP than in the other treatments. Dissolution of TSP causes direct soil acidification (Lindsay, 1979). Triple superphosphate, which contains monocalcium phosphate [$Ca(H_2PO_4)_2 \cdot H_2O$], dissociates H^+ ion from the $H_2PO_4^-$ molecule and generates acidity which leads to higher PRP in the center section than the RNP and control. Soil acidification by MAP could persist longer than TSP due to the indirect nature of acidification (Heronemus et al., 2021).

Even though the RNP reduced soil pH, the center section PRP was the lowest. This lowest PRP could be due to strong P sorption on to Fe and Al in the RNP. The adsorption reactions of P onto surfaces may be mono- or bidentate, as inner-sphere complexes, or as an outer-sphere complex (Essington, 2003). According to Sposito, 1989, most adsorbed P in soil occurs as inner-sphere complex species (specific adsorption), and some P is adsorbed as either diffuse ion swarm or outer-sphere complex species (nonspecific adsorption). The strong P sorption reduces the available P to plants. Several studies have also shown that iron phosphates, including vivianite, act as P sinks in soils (Nieminen et al., 2011; Saracanlao et al., 2023). The Al or Fe oxide-containing drinking water treatment residuals (WTRs), a by-product of municipal drinking water treatment plants, can also adsorb tremendous amounts of P (Ippolito et al., 2003). Heil, 1989 observed severe P-deficiency symptoms in sorghum–sudangrass when applied 25 g WTR kg^{-1} soil WTR application. Elliott, 1988 and Bugbee & Frink 1985 found reduced P concentrations in tomato and lettuce grown in WTR-amended potting media. This RNP could be used as a P sink in this tested soil as it reduced the plant's available P after application.

Short-term laboratory, greenhouse, and rainfall simulation studies have demonstrated WTR efficacy in reducing soluble P concentrations in runoff (Dayton et al., 2003; Dayton & Basta, 2005a; Elliott et al., 2005) and leachate (Elliott et al., 2002) from areas amended with

animal manure. This shows that WTRs could be used to remove dissolved phosphorus from agricultural runoff water, which can significantly improve the overall quality of surface water as an effective Best Management Practice (BMP). Novak & Watts, 2004 found that applying WTR decreases the amount of P available for off-site transport and reduces the extractable soil P concentrations in soil with excessive P concentrations. A field study amendment with Al-WTR reduced water-soluble P concentration compared to the control plots by ≥60%, and the WTR-immobilized P remained stable for 7.5 yr. under field conditions (Agyin-Birikorang et al., 2007). Applications of WTR with higher P sorption maximum values could be a part of BMP for biosolids or manure field applications (Ippolito et al., 2011).

Summary

The P diffusion and percent resin extractable P results demonstrated that P in RNP was not mobile or resin extractable compared to conventional fertilizers, MAP and TSP, in the selected mildly calcareous soil. As physical and chemical heterogeneity may lead to differences in the fertilizer value of the recovered products, a modified AnMBR associated nutrient recovery process could lead to RNPs with higher total P% and more solubility. This current study on the RNP showed that this Fe- based RNP was not an effective fertilizer but acted as a P sink in specific agricultural systems where the low solubility is beneficial. It could be helpful when excessive dissolved reactive P runoff threatens the ecosystem via eutrophication, hypoxic zones, and harmful algal blooms in surface waters from land-applied P. More research is required to enhance the understanding of the behavior of the RNPs in various soil types. Furthermore, it is essential to improve the efficiency of removing these products and to ensure that the precipitate characteristics are consistent and predictable, which leads to the optimal operation of wastewater

treatment systems. The results will implement P recovery from waste streams and beneficial reuse of P in agricultural production.

References

Agyin-Birikorang, S., G.A. O'connor, L.W. Jacobs, K.C. Makris, and S.R. Brinton. 2007. Long term phosphorus immobilization by a drinking water treatment residual. J. Environ. Qual. 36: 316–323

Ali, A., Y.W. Chiang, and R.M. Santos. 2022. X-ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions. Minerals. 12: 205. https://doi.org/10.3390/min12020205

Babic-Ivancic, V., J. Contrec, D. Kralj, and L. Brecevic. 2002. Precipitation diagrams of struvite and dissolution kinetics of different struvite morphologies. Croat. Chem. Acta. 75: 89–106.

Baig, A.A., J.L. Fox, R.A. Young, Z. Wang, J. Hsu, W.I. Higuchi, A. Chhettry, H. Zhuang, and M. Otsuka. 1999. Relationships among carbonated apatite solubility, crystallite size, and microstrain parameters. Calcif. Tissue Int. 64: 437-449.

Bashar, R., K. Gungor, K.G. Karthikeyan, and P. Barak. 2018. Cost effectiveness of phosphorus removal processes in municipal wastewater treatment. Chemosphere. 197: 280–290.

Battistoni, P., A. De Angelis, P. Pavan, M. Prisciandaro, and F. Cecchi. 2001. Phosphorus removal from a real anaerobic supernatant by struvite crystallization. Water Res. 35: 2167–2178.

Bindraban, P.S., C. O. Dimkpa and R. Pandey. 2020. Exploring phosphorus fertilizers and fertilization strategies for improved human and environmental health. Biol. Fertil. Soils. 56: 299–317. https://doi.org/10.1007/s00374-019-01430-2

Bowers, K.E., T. Zhang, and J.H. Harrison. 2007. Phosphorus removal by struvite crystallization in various livestock wastewaters. In: Proceedings of International Symposium on Air Quality and Waste Management for Agriculture. American Society of Agricultural and Biological Engineers Meeting Paper No. 701P0907cd. St. Joseph, Mich., ASABE.

Breckenridge, R.P., and A.B. Crockett. 1998. Determination of background concentrations of inorganics in soils and sediments at hazardous waste sites. Environ. Monit. Assess. 1998 (51): 621–656. https://doi.org/10.1023/A:1005808031053.

Bugbee, G.J., and C.R. Frink. 1985. Alum sludge as a soil amendment: Effects on soil properties and plant growth. Bull. 823. Connecticut Agric. Exp. Stn., New Haven.

Cordell, D., A. Rosemarin, J.J Schröder, and A. L. Smit. 2011. Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options. Chemosphere. 4(6): 747–758. https://doi.org/10.1016/j.chemosphere.2011.02.032

Cordell, D., and S. White. 2013. Sustainable Phosphorus Measures: Strategies and Technologies for Achieving Phosphorus Security. Agronomy. 3(1): 86–116. https://doi.org/10.3390/agronomy3010086

Cunha, J. R., C. Schott, R. D. Van der Weijden, L.H. Leal, G. Zeeman, and C. Buisman, 2020. Calcium phosphate granules recovered from black water treatment: A sustainable substitute for mined phosphorus in soil fertilization. Resour Conserv Recycl. 158: 104791. https://doi.org/10.1016/j.resconrec.2020.104791.

Dayton, E.A., and N.T. Basta. 2005. Use of drinking water treatment residuals as a potential best management practice to reduce phosphorus risk index scores. J. Environ. Qual. 34: 2112–2117.

Dayton, E.A., N.T. Basta, C.A. Jakober, and J.A. Hattey. 2003. Using treatment residuals to reduce phosphorus in agricultural runoff. J. Am. Water Works Assoc. 95: 151–158.

Elliott, H.A. 1988. Effect of water treatment sludge on growth and elemental composition of tomato shoots. Commun. Soil Sci. Plant Anal. 19: 345–354. https://doi.org/10.1080/00103628809367943

Elliott, H.A., G.A. O'Connor, and S. Brinton. 2002. Phosphorus leaching from biosolids-amended sandy soils. J. Environ. Qual. 31: 1362–1369. https://doi.org/10.2134/jeq2002.1362

Elliott, H.A., R.C. Brandt, and G.A. O'Connor. 2005. Runoff phosphorus losses from surface-applied biosolids. J. Environ. Qual. 34: 1632–1639. https://doi.org/10.2134/jeq2004.0467

Essington, M. E., 2015. Soil and Water Chemistry: An Integrative Approach. CRC press.

Godfray, H. C. J., J.R. Beddington, I.R. Crute, L. Haddad, D. Lawrence, and J.F. Muir. 2010. Food security: The challenge of feeding 9 billion people. Science. 327: 812–818.

Gutierrez, O., D. Park, K.R. Sharma, and Z. Yuan. 2010. Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment. Water Res. 44(11): 3467–3475. https://doi.org/10.1016/j.watres.2010.03.023

Hanson, R.L., and D.G. Westfall. 1985. Orthophosphate solubility transformations and availability from dual applied nitrogen and phosphorus. Soil Sci. Soc. Am. J. 49:1283–1289.

Hedley, M., and M. McLaughlin. 2005. Reactions of Phosphate Fertilizers and By-Products in Soils, in Sims, T. J., Sharpley, A. N. (eds.): Phosphorus: Agriculture and the Environment. ASA, CSSA, SSSA, Madison, WI, USA. 181–251.

Heil, D.M. 1989. Water treatment sludge influence on the growth of sorghum–sudangrass. J. Environ. Qual. 18: 292–298.

Heronemus, E., K. H.H. Gamage, G. M. Hettiarachchi, and P. Parameswaran. 2021. Efficient recovery of phosphorus and sulfur from Anaerobic Membrane Bioreactor (AnMBR) permeate using chemical addition of iron and evaluation of its nutrient availability for plant uptake. Sci. Total Environ. 783: 146850. https://doi.org/10.1016/j.scitotenv.2021.146850.

Hettiarachchi, G.M., E. Lombi, M. McLaughlin, D. Chittleborough, and C. Johnston. 2010. Chemical behavior of fluid and granular Mn and Zn fertilisers in alkaline soils. Soil Res. 48: 238–247.

Hettiarachchi, G.M., E. Lombi, M.J. McLaughlin, D. Chittleborough, and P. Self. 2006. Density changes around phosphorus granules and fluid bands in a calcareous soil. Soil Sci. Soc. Am. J. 70: 960-966.

Hettiarachchi, G.M., E. Lombi, M.J. McLaughlin, D.J. Chittleborough, and C. Johnston. 2010. Chemical behavior of fluid and granular Mn and Zn fertilisers in alkaline soils. Aust. J. Soil Res. 48: 238–247.

Hettiarachchi, G.M., M.J. McLaughlin, K.G. Scheckel, D.J. Chittleborough, M. Newville, S. Sutton, and E. Lombi. 2008. Evidence for different reaction pathways for liquid and granular micronutrients in a calcareous soil. Soil Sci. Soc. Am. J. 72: 98–110.

Huang, X. L., Y. Chen, and M. Shenker. 2012. Dynamics of phosphorus phytoavailability in soil amended with stabilized sewage sludge materials. Geoderma. 170: 144–153.

Ippolito, J.A., K.A. Barbarick, and H.A. Elliott. 2011. Drinking water treatment residuals: a review of recent uses. J. Environ. Qual. 40: 1–12.

Ippolito, J.A., K.A. Barbarick, D.M. Heil, J.P. Chandler, and E.F. Redente. 2003. Phosphorus retention mechanisms of a water treatment residual. J. Environ. Qual. 32: 1857–1864.

Klammsteiner, T., V. Turan, M. Fernandez-Delgado Juarez, S. Oberegger, and H. Insam. 2020. Suitability of Black Soldier Fly Frass as soil amendment and implication for organic waste hygienization. Agronomy. 10(10): 1.

Klug, H.P. and Alexander, L.E. 1974. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. John Wiley & Sons, New York.

Le Corre, K.S., E. Valsami-Jones, P. Hobbs, and S.A. Parsons. 2007. Impact of reactor operation on success of struvite precipitation from synthetic liquors. Environ. Technol. 28: 1245–1256.

Lei, Y., B. Song, R.D. van der Weijden, and M. Saakes, and C.J.N. Buisman. 2017. Electrochemical Induced Calcium Phosphate Precipitation: Importance of Local pH. Environ. Sci. Technol. 51(19): 11156–11164. https://doi.org/10.1021/acs.est.7b03909

Liao, B.-Q., J.T. Kraemer, and D.M. Bagley. 2006. Anaerobic Membrane Bioreactors: Applications and Research Directions. Crit Rev Environ Sci Technol. 36(6): 489–530. https://doi.org/10.1080/10643380600678146

Lim, K., P.J. Evans, and P. Parameswaran. 2019. Long-Term Performance of a Pilot-Scale Gas-Sparged Anaerobic Membrane Bioreactor under Ambient Temperatures for Holistic Wastewater Treatment. Environ. Sci. Technol. 53(13): 7347–7354. https://doi.org/10.1021/acs.est.8b06198

Lin, H., W. Peng, M. Zhang, J. Chen, H. Hong, and Y. Zhang. 2013. A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives. Desalination. 314: 169–188. https://doi.org/10.1016/j.desal.2013.01.019

Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Lombi, E., M.J. McLaughlin, C. Johnston, R.D. Armstrong, and R.E. Holloway. 2004. Mobility and Lability of phosphorus from granular and fluid Monoammonium phosphate differs in a calcareous soil. Soil Sci. Soc. Am. J. 68: 682–689.

Ma W. Q., L. Ma, J.H. Li, F.H. Wang, I. Sis´ak, and F.S. Zhang. 2011. Phosphorus flows and use efficiencies and consumption of wheat, rice, and maize in China. Chemosphere. 84: 814–821.

Massey, M.S., 2019. X-ray spectroscopic quantification of Struvite and Dittmarite recovered from wastewater. J. Environ. Qual. 48: 193–198.

Massey, M.S., I. Zohar, J.A. Ippolito, and M.I. Litaor. 2018. Phosphorus sorption to aluminum based water treatment residuals reacted with dairy wastewater: 2. X-ray Absorption Spectroscopy. J. Environ. Qual. 47:546–553.

Massey, M.S., J.A. Ippolito, J.G. Davis, and R.E. Sheffield. 2010. Macroscopic and microscopic variation in recovered magnesium phosphate materials: implications for phosphorus removal processes and product re-use. Bio resour. Technol. 101: 877–885.

Mayer, B. K., L. A. Baker, T. H. Boyer, P. Drechsel, M. Gifford, M. A. Hanjra‖, P. Parameswaran, J. Stoltzfus, P. Westerhoff, and B. E. Rittmann. 2016. Total Value of Phosphorus Recovery. Environ. Sci. Technol. 50(13) 6606–6620. https://doi.org/10.1021/acs.est.6b01239

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27: 31-36.

Myers, R.G., A.N. Sharpley, S.J. Thien, and G.M. Pierzynski. 2005. Ion-sink phosphorus extraction methods applied on 24 soils from the continental USA. Soil Sci. Soc. Am. J. 69: 511-521.

Novak, J.M. and D.W. Watts. 2004. Increasing the phosphorus sorption capacity of southeastern coastal plain soils using water treatment residuals. Soil Sci. 169: 206–214.

Olsen, S.R., and F.S. Watanabe. 1963. Diffusion of phosphorus as related to soil texture and plant uptake. Soil Sci. Soc. Amer. Proc. 27: 648-653.

Pierzynski, J. and G.M. Hettiarachchi. 2018. Reactions of phosphorus fertilizers with and without a fertilizer enhancer in three acidic soils with high phosphorus-fixing capacity. Soil Sci. Soc. Am. J. 82:1124-1139.

Rafullah, K.M., D. Muhammad, S. Fahad, M. Adnan, F. Wahid, S. Alamri, F. Khan, K. Dawar, I. Irshad, S. Danish, M. Arif, S.S. Amanullah, B. Khan, I. Mian, R. Datta, T. Zarei, A. Shah, M. Ramzan, M. Zafar-ul-Hye, M. Mussarat, and M. Siddiqui. 2020. Phosphorus nutrient management through synchronization of application methods and rates in wheat and maize crops. Plants 9(10):1. https://doi.org/10.3390/plants9101389

Ranatunga, T. D., S.S. Reddy, and R.W. Taylor. 2013. Phosphorus distribution in soil aggregate size fractions in a poultry litter applied soil and potential environmental impacts. Geoderma.192: 446–452.

Raynaud, S., E. Champion, D. Bernache-Assollant, and P. Thomas. 2002. Calcium phosphate apatites with variable Ca/P atomic ratio I. synthesis, characterization, and thermal stability of powders. Biomaterials. 23: 1065-1072.

Robles, Á., D. Aguado, R. Barat, L. Borrás, A. Bouzas, J.B. Giménez, N. Martí, J. Ribes, M.V. Ruano, J. Serralta, J. Ferrer, and A. Seco. 2020. New frontiers from removal to recycling of nitrogen and phosphorus from wastewater in the Circular Economy. Bioresour. Technol. 300: 122673–122673. https://doi.org/10.1016/j.biortech.2019.122673

Rothe, M., A. Kleeberg, and M. Hupfer. 2016. The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments. Earth Sci Rev. 158: 51–64. https://doi.org/10.1016/j.earscirev.2016.04.008

Roychand, R., B. Kumar Pramanik, G. Zhang, and S. Setunge. 2020. Recycling steel slag from municipal wastewater treatment plants into concrete applications – A step towards circular economy. Resour Conserv Recycl. 152: 104533. https://doi.org/10.1016/j.resconrec.2019.104533

Saggar, S., M.J. Hedley, and R.E. White. 1990. A simplified resin membrane technique for extracting phosphorus from soils. Fert. Res. 24: 173–180.

Saracanlao, R.J., H. Van Ryckel, M. Verbeeck, M. Everaert, E. Smolders. 2023. Increasing phosphorus fertilizer value of recycled iron phosphates by prolonged flooding and

organic matter addition. Pedosphere. ISSN 1002-0160. https://www.sciencedirect.com/science/article/pii/S1002016023000395

SAS Institute. 2011. The SAS System for Windows Version 9.1.3. SAS Institute, Cary, NC.

Scholz R. W. and F.W. Wellmer. 2013. Approaching a dynamic view on the availability of mineral resources: What we may learn from the case of phosphorus?. Global Environ Chang. 23: 11–27.

Schroder J. J., A.L. Smit, D. Cordell, and A. Rosemarin. 2011. Improved phosphorus use efficiency in agriculture: A key requirement for its sustainable use. Chemosphere. 84: 822–831.

Schroder, J.J., D. Cordell, A.L. Smit, and A. Rosemarin, 2010. Sustainable use of phosphorus: EU tender ENV.B1/ETU/2009/0025 357. Biosyst Eng. https://library.wur.nl/WebQuery/wurpubs/404463

Sharpley, A., and H. Tunney. 2000. Phosphorus research strategies to meet agricultural and environmental challenges of the 21st Century. J. Environ. Qual. 29: 176-181.

Smil, V. 2000. Phosphorus in the environment: natural flows and human interferences. Annu Rev Energy Environ. 25: 53–88

Sohrt J., F. Lang, and M. Weiler. 2017. Quantifying components of the phosphorus cycle in temperate forests. Wiley Interdiscip Rev Water. 4: e1243

Sonmez, O., V. Turan, and C. Kaya. 2016. The effects of sulfur, cattle, and poultry manure addition on soil phosphorus. Turk. J. Agric. For. 40, 536–541.

Sposito, G. 1989. The Chemistry of Soils. xiii 277 pp. New York, Oxford: Oxford University Press. ISBN 0 19 504615 3.

Stratful, I., M.D. Scrimshaw, and J.N. Lester. 2001. Conditions influencing the precipitation of magnesium ammonium phosphate. Water Res. 35: 4191–4199.

Taalab, A.S., G.W. Ageeb, S. Siam Hanan, and A. Mahmoud Safaa. 2019. Some characteristics of calcareous soils: a review. Middle East J Agric Res. 8(1): 96–105.

Tchobanoglous, G., H.D. Stensel, R. Tsuchihashi, F.L. Burton, M. Abu-Orf, G. Bowden, and W. Pfrang. 2014. Wastewater Engineering: Treatment and Resource Recovery. 5th edition. McGraw Hill, New York, N.Y.

Turan, V., P. Schröder, S. Bilen, H. Insam, and M. Fernández-Delgado Juárez. 2019. Coinoculation effect of Rhizobium and Achillea millefolium L. oil extracts on growth of common bean (Phaseolus vulgaris L.) and soil microbial-chemical properties. Sci. Rep. 9 (1) (15178-10).

USEPA. 2007. Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils and oils. Test methods. USEPA. http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3051a.pdf

Vogel, T., J. Kruse, N. Siebers, M. Nelles, and B. E. Löbermann. 2017. Recycled Products from Municipal Wastewater: Composition and Effects on Phosphorus Mobility in a Sandy Soil. J. Environ. Qual. 46: 443–451.

Walan, P., S. Davidsson, S. Johansson, and M. H¨o¨ok. 2014. Phosphate rock production and depletion: regional disaggregated modeling and global implications, Resour. Conserv. Recycl. 93: 178–187, https://doi.org/10.1016/j.resconrec.2014.10.011.

Wang, L., and G.H. Nancollas. 2008. Calcium Orthophosphates: Crystallization and Dissolution. Chem. Rev. 108(11): 4628–4669. https://doi.org/10.1021/cr0782574

Weeks, J.J., and G.M. Hettiarachchi. 2020. Source and formulation matter: new insights into phosphorus fertilizer fate and transport in mildly calcareous soils. Soil Sci. Soc. Am. J. 84: 731–746.

Wilfert, P., A.I. Dugulan, K. Goubitz, L. Korving, G.J. Witkamp, and M.C.M Van Loosdrecht. 2018. Vivianite as the main phosphate mineral in digested sewage sludge and its role for phosphate recovery. Water Res. 144: 312–321. https://doi.org/10.1016/j.watres.2018.07.020

Wu, H., A. Ikeda-Ohno, Y. Wang, and T.D. Waite. 2015. Iron and phosphorus speciation in Fe-conditioned membrane bioreactor activated sludge. Water Res. 76: 213–226. https://doi.org/10.1016/j.watres.2015.02.020

Zhang, X. D., H. Spanjers, and J.B. van Lier. 2013. Potentials and limitations of biomethane and phosphorus recovery from sludges of brackish/marine aquaculture recirculation systems: A review. J Environ Manage. 131: 44–54.

Zhang, X., E.A. Davidson, T. Zou, L. Lassaletta, Z. Quan, T. Li, and W. Zhang. 2020. Quantifying Nutrient Budgets for Sustainable Nutrient Management. Global Biogeochem Cycles. 34(3).

Zohar, I., M.S. Massey, J.A. Ippolito, and M.I. Litaor. 2018. Phosphorus sorption to aluminum-based water treatment residuals reacted with dairy wastewater: 1. Isotherms, XRD, and SEM-EDS analysis. J. Environ. Qual. 47: 538–545.

Chapter 4 - Recovered calcium based-phosphorus products from animal wastewater: Fate and behavior in soils

Abstract

Phosphorus (P) is a vital crop nutrient. The increasing demand for P sources and concerns about surface water quality raises the need to explore safe and efficient secondary P fertilizer sources from wastewater. Recovered nutrient products (RNPs) from wastewater may contain high concentrations of plant-available nutrients. Thus, they can be effective alternative fertilizers. This study evaluated the effectiveness of Ca-based RNP from synthetic swine wastewater using an innovative anaerobic membrane bioreactor (AnMBR) technology. This study aimed to characterize the RNP and compare the dissolution, transformations, and potential bioavailability of P in RNP with conventional P fertilizers in selected calcareous, neutral, and acidic soils using short-term laboratory incubation studies. Soils were incubated for 3 days, 1 week, and 5 weeks in Petri dishes with four treatments: RNP, monoammonium phosphate (MAP), triple superphosphate (TSP), and control. After each period, soils were sectioned at different distances from the point of application, and soil pH, total P to assess P diffusion, and resin extractable P to assess potential plant-available P were measured. Selected samples were also analyzed using X-ray absorption near edge structure (XANES) spectroscopy to identify the P speciation in tested soils. P diffuses from the center section to the next section for all the tested soils in all treatments. Resin extractable P (% of total) also increased during the study period. Phosphorus reaction products further showed differences in P speciation in different treatments in tested soils. The results showed that Ca-based RNP acted as a P source for tested soils and showed a lower solubility and extractability than conventional fertilizers. Modification to Ca-based RNP recovery may offer useful secondary P sources for agriculture.

Introduction

Phosphorus (P) is an essential macro element for all life forms. Sedimentary phosphate rock, the primary P source in agriculture, is finite (Cunha et al., 2020). The demand for P sources increases with the growing world population, and the global P scarcity is expected to be one of the greatest barriers to food production in the 21st century, given its dependence on the mining of non-renewable phosphate rock (Cordell et al., 2011). Thus, economically extractable rock phosphate will eventually become scarce as it is exploited at higher rates. The cost of P fertilizer increased to 800% during the 2008 economic crisis, in addition to future food security threats (Cordell & White, 2013). It has been suggested that P demand will peak above P supply before 2040 (Cordell & White, 2013). Further, applying nutrients to agricultural systems has resulted in a remarkable increase in yield, and overloading nutrients to soils leads to environmental concerns such as eutrophication, harmful algal blooms, and hypoxic zones in surface waters. Therefore, sustainable management of nutrients in agricultural systems has become a grand challenge for the 21st century (Zhang et al., 2020). Agricultural production has been identified as a significant source of sediment nitrogen (N) and P pollution, leading to surface water quality issues (Sharpley & Tunney, 2000). The increase in P pollution to surface water is especially detrimental, although not exclusive, to freshwater bodies (Moody, 2011). Therefore, the increasing demand for P sources and concerns about surface water quality raises the need to explore safe and efficient secondary P fertilizer sources.

Wastewater contains nutrients such as P and N that can be recovered for fertilizer production, water that can be reused, and energy potential that can be harnessed from organic matter (Robles et al., 2020). Therefore, there is an increased focus on wastewater as part of the circular economy (Robles et al., 2020; Roychand et al., 2020). Many treatment plants are

beginning to brand themselves as Water Resource Recovery Facilities (WRRFs), representing a paradigm shift within the water sector. Harvesting nutrients and energy from wastewater treatment technologies builds new, important interrelationships between food, energy, and water systems. Several secondary phosphate resources of plant and animal origin have already been considered valuable P sources for plant production (Vogel et al., 2017). Swine waste, as wastewater or manure, has excellent potential to display the circular economy concept as it contains higher organic and nutrient concentrations with a chemical oxygen demand (COD) that can be upwards of 10,000 mg/L and P and N concentrations that can be as high as 250 mg/L P and 1200 mg/L N (Cheng et al., 2020). As this is about ten times the strength of municipal wastewater (Henze et al., 2008), there is a greater potential for energy recovery through biogas production from anaerobic processes and potential nutrient sequestration (Cheng et al., 2020; Meinen et al., 2014).

The behavior of P added in waste products to soil depends on the chemical composition and physical characteristics of the waste and soil properties (Velthof et al., 1998; Hedley & McLaughlin, 2005; Brod et al., 2015a). Sewage wastes and animal manures generally have lower total and water-soluble P concentrations than mineral P fertilizers and contain varying amounts of organic P and other elements that may affect P availability to plants (Hedley & McLaughlin, 2005). Also, recovered products from waste streams cause the potential presence of heavy metals, organic micropollutants, and pathogens, which raises concerns (Cunha et al., 2020). Anaerobic membrane bioreactors represent an emerging environmental biotechnology platform with the potential to simultaneously recover water, energy, and nutrients from various concentrated wastewater (Liao et al., 2006; Lin et al., 2013). This technology combines the techniques of anaerobic biological treatment and membrane filtration. A pilot-scale gas sparged

AnMBR successfully operating at Swine unit, Kansas State University and treats wastewater with the seasonally varying temperature that includes dissolved methane recovery using a membrane contactor, sulfide and P recovery using coagulation, flocculation, and sedimentation and ammonia capture using a clinoptilolite column (Lim et al., 2019).

The tailored P applications by RNPs reduce food and water quality deterioration from land application of livestock wastewaters and could make agriculture production more sustainable, economical, and environmentally friendly. Recent studies have focused on the P recovery process, and some evidence exists that recovered struvite might be a good fertilizer (Lindsay, 1979; Johnston & Richards, 2003; Li & Zhao, 2003; Massey et al., 2009; Rech et al., 2018). Plant availability of recycled P products derived from dairy effluents and pig manures was evaluated using pot and soil incubation experiments by Achat et al., 2014. Many other studies assess the total P and further characterize the recovered products (Massey et al., 2009; Massey et al., 2010; Cunha et al., 2020; Szogi et al., 2018). Minimal data are available regarding the potential use of these RNPs in soils. Therefore, the overall aims of this study were to characterize and compare the Ca-based RNPs recovered from synthetic swine wastewater using an innovative anaerobic membrane bioreactor (AnMBR) technology. Dissolution, transformations, and potential bioavailability of P in RNPs were investigated with conventional P fertilizers in selected calcareous, neutral, and acidic soils using short-term laboratory incubation studies combined with wet chemical and synchrotron-based x-ray techniques.

Materials and Methods

Recovered nutrient product recovery

A synthetic swine media was prepared based on previous studies of swine waste treatment. This was to simulate the permeate after swine waste treatment through the AnMBR.

The media composition was 378 mg/L NH_4^+-N, 342 mg/L K, 21 mg/L Mg, 39 mg/L Ca, 0.9 mg/L Fe, and a 50 mM borate buffer and 30 mg/L of dissolved sodium sulfide (Raby et al., 2013). Based on a 90% removal rate achieved in the pilot-scale gas-sparged AnMBR treating municipal wastewater, 1080 mg/L of COD was added as 154.2 mg/L propionic acid, 146.4 mg/L acetic acid, 300 mg/L lactic acid, 7 mg/L butyric acid, and 170 mg/L ethanol (Huang et al., 2015). The phosphate concentration was 50 mg/L, and the pH was increased to the appropriate level for using 5 *M* sodium hydroxide (Heronemus, 2021).

Product characterization

A semi-solid nutrient-rich sample obtained from synthetic swine permeate was freeze-dried and digested using USEPA method SW846-3051A (USEPA, 2007) in a microwave digestion unit. The nutrient composition and selected potentially toxic trace elements in the digestate were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, 720-ES, Varian, Santa Clara, CA) and an inductively coupled plasma mass spectrometer (ICP-MS, 7500cx, Agilent, Santa Clara, CA). The pH of the freeze-dried product was measured in a 1:10 product: water extract. The 2% (w/v) citric acid solubility analysis was conducted using a modified method used by the Association of Official Agricultural Chemists, 1945 for freeze-dried products. Citric acid solubility is used to identify the fertilizer value of the product. A powder X-ray diffraction (XRD) analysis was done to identify existing nutrient phases in the RNP using PANalytical Empyrean Multi-Purpose X-Ray Diffractometer (Spectris Company, Egham, Surrey, UK) using Cu Kα radiation at a wavelength of 1.54 Å and generator settings of 45 kV and 40 mA. Measurements were made using a continuous scanning technique from 5 to 70 °2θ and a scan speed of 0.024° per second. Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectroscopy analysis was also performed using a Hitachi S-

3500 N scanning electron microscope equipped with a Model S-6542 absorbed electron detector (Hitachi Science Systems, Ibaraki, Japan) at an accelerating potential of 5 kV. Further product characterization was done using X-ray absorption near-edge structure (XANES) spectroscopy at Sector 9-BM-B, Advanced Photon Source, Argonne National Laboratory, Argonne, IL. The RNP sample was diluted ten times using boron nitride to avoid self-absorption issues. A KBr Quick Press Kit (International Crystal Laboratories, Garfield, NJ) was used to make pellets of the RNP sample and carefully placed on a double-sided carbon tape (SPI Supplies, West Chester, PA), then on the sample holder and placed into a helium filled chamber for analysis. In fluorescence mode, six XANES scans were collected for the sample at a range of 2.1 to 2.4 keV. All spectra, including the P_2O_5 standard used for energy calibration, were collected with a solid-state drift detector.

Edge energy was calibrated using phosphorus pentoxide (P_2O_5) and the background correction followed by the linear combination fitting of the reported spectra was done using in Athena (Ravel & Newville, 2005) according to the concepts of Werner and Prietzel (2015). Previously collected P reference standards were also used, and the P_2O_5 standard spectra were collected during each run for any energy shifts.

Transformations, reaction pathways, and availability of RNP in soils

Three contrasting soils were sampled for the short-term laboratory incubation studies, calcareous soil from Garden city Kansas, USA, acidic soil (an Oxisol) from Bahia, Brazil, and a neutral soil (a Mollisol) from Manhattan, Kansas, USA. Soils were collected at a 0-15 cm depth, air-dried, and sieved to <2mm. The pH of the soil was measured in a 1:10 soil: water extract (Watson & Brown, 1998). The cation exchange capacity (CEC) was determined by the displacement method (Soil Survey Staff, 2011). Carbonates were determined according to

Allison & Moodie, 1965. The total P was determined using Zarcinas et al., 1996, which was modified to use a digestion block instead of a microwave. Available P was measured by extraction with sodium bicarbonate (Olsen, 1954) for the calcareous soil, and Mehlich-3 P was determined as described in Frank et al., 1998 for neutral and acidic soils. Total organic C and total N were determined via dry combustion method by Nelson & Sommers, 1996. Soil texture was determined using a combination of a modification of the pipette method by Kilmer & Alexander, 1949 and Method 3A-1 from the Soil Survey Laboratory's methods manual (Soil Survey Laboratory Staff, 2004). The maximum water-holding capacity was measured using the protocol from Jenkinson & Powlson, 1976. Petri dishes (87 mm diameter and 11 mm height) were packed with a pre-moist soil to a bulk density of 1.0 g cm^{-3}, 1.0 g cm^{-3}, 1.1 g cm^{-3}, respectively, for calcareous, neutral, and acid soils. Then added the remaining moisture to achieve 55%, 60%, and 50% of soil's maximum water-holding capacity respectively for calcareous, neutral and acidic soils. Desired water-content was achieved by adding remaining deionized water slowly onto the packed soil. Preliminary work showed that these bulk densities were ideal for filling the volume of the petri dish without unnecessary compression. The plates were wrapped with Parafilm (Bemis Flexible Packaging, Neenah, WI) and left to equilibrate for 24 h at room temperature. The plates were unwrapped. Then the powdered treatments were placed in the center of the plate, just below the soil surface, and covered with soil. There were four treatments with four replicates as follows:

i. Unfertilized control soil sample;

ii. Monoammonium phosphate (MAP, 11:23:0; 11% N–23% P–0% K2O by weight): 7.5 mg P;

iii. Triple superphosphate (TSP, 0:20:0; 0% N–20% P–0% K2O by weight): 7.5 mg P; and

iv. RNP (11.5% P by weight): 7.5 mg of P.

Petri dishes were closed, wrapped individually with Parafilm and stacked. Then stacked dishes were wrapped in aluminum foil and incubated (Precision Low Temp Incubator, Waltham, MA) in the dark at 25 °C. Each study for calcareous and acid soil was conducted for three incubation periods of 3-days, 1-week, and 5-weeks. and Each study for neutral soil was conducted for two incubation periods as 1-week and 5- weeks. Each study consisted of 3 and 2 separate sets per soil respectively. Plates were opened at the end of each period. The soil was collected from 0 to 7.5, 7.5 to 13.5, 13.5 to 25, and 25 to 43.5mm, from the point of application as concentric rings starting from the center. Each sample was placed in a pre-weighed plastic specimen container (Fisher Scientific, Waltham, MA). The samples were oven-dried quickly at 40 °C (Fisher Scientific drying oven, Waltham, MA). After drying, weight was recorded, and soils were ground gently with a mortar and pestle.

Total P for all samples was determined by aqua regia digestion (without H_2O_2 pretreatment) and analyzed via ICP-OES. Total P data were normalized by calculating the percentage of P added (PPA) for each dish section for all treatments (Hettiarachchi et al., 2010) is defined as follows:

$$PPA = \frac{(P_f)S_i \times M_i}{\sum_{i=1-4}[(P_f)S_i \times M_i]} \times 100$$

where *i* is the dish section (1–4), (P_f)*S*i is the concentration of P fertilizer in each dish section, and *M*i is the mass of soil in each dish section. (P_f)*S*i is calculated by subtracting the total P concentration of the unfertilized soil sample from the total P concentration in the fertilized dish section.

Potentially plant available P was determined by the anion exchange resin (AER) technique (Myers et al., 2005) and quantified colorimetrically using a Beckman-Coulter DU-800

spectrophotometer (Brea, CA) (Murphy and Riley, 1962). Percentage of resin extractable P (PRP) for each dish section for all treatments were calculated according to the following equation (Pierzynski & Hettiarachchi, 2018):

$$PRP = \frac{REP_i}{Total\ P_i} \times 100$$

where i is the dish section (1–4), REP_i is the resin P concentration, and $Total\ P_i$ is the total P concentration in the i^{th} dish section.

X-ray absorption near-edge structure analysis was performed for the composite samples of the 0- to 7.5 mm, and 7.5-13.5 mm sections, prepared using equal masses of soil from the four replicates used for chemical analysis. The P K-edge XANES data were collected at Sector 9-BM-B, Advanced Photon Source, Argonne National Laboratory, Argonne, IL. All spectra, including the P_2O_5 standard used for energy calibration, were collected with a solid-state drift detector in fluorescence mode. A 7-mm soil pellet was prepared from the soil with the KBr Quick Press Kit (International Crystal Laboratories, Garfield, NJ) and carefully mounted on the sample holder with double-sided carbon tape (SPI Supplies, West Chester, PA) and placed into a helium filled chamber for analysis. Six scans were collected for each P treated sample, and 12 scans were collected for each control sample at a range of 2.1 to 2.4 keV.

Background correction and linear combination fitting of the experimental spectra were completed in Athena (v.0.9.25) (Ravel & Newville, 2005) according to the concepts set forth by Werner & Prietzel, 2015. Previously collected P reference standards were also used, and the P_2O_5 standard spectra were collected during each run for spectral alignment. Briefly, three or four scans were merged to limit noise. Pre-edge and normalization ranges were not fixed, allowing for each sample's maximized fit. All spectra were adjusted such that E_0 of 2149 eV

corresponded to one-half the height of the white line peak. Reference spectra were eliminated if they comprised <5% of the calculated composition and the fitting was repeated.

Statistical analysis

All soil data were analyzed in SAS (SAS Institute, 2011) through the Proc MIXED procedure. The experimental design was a complete randomized design. Data were analyzed via ANOVA with P fertilizer treatment as the main treatment, and dish sections as subplot treatments. The Tukey's HSD test was used to compare all treatments at an $p = 0\ .05$ level of significance.

Results and Discussion

Characterization of the recovered nutrient product

The RNP was rich in Ca, and P, comprising approximately 34% and 11.5%, respectively and the measured trace element concentrations were low (Table 4.1). Product pH (1:10 product: water) was 8.5, alkaline. Significant amounts of Ca in this RNP were predominantly from the calcium salts used for P precipitation. The addition of calcium oxide during the production process of this synthetic swine permeates forms calcium hydroxide, releasing both calcium and hydroxide ions. The hydroxide ions are essential for the formation of several crystalline forms of calcium phosphate, as well as for increasing the pH. It has been observed empirically that higher pH causes calcium phosphate products to precipitate more readily (Lei et al., 2017; Tran et al., 2014; Wang & Nancollas, 2008).

The 2% (w/v) citric acid solubility (as a % of total P) of this RNP was 3%. This could be due to the residual alkalinity and the level of crystallinity in the product. Citric acid solubility is used to identify the fertilizer value of the product. As a reference, soft rock phosphate's 2% citric acid solubility is about 30%, and TSP is about 88% of total P (Christiansen et al., 2020). The

crystallinity of the products and the substitution of ions such as Al and Fe affect the 2% citric acid solubility (Braithwaite & Eaton, 1990).

Table 4.1. Selected major and trace elemental composition of the recovered nutrient product.

Major Element[†]	**Concentration% (w/w)**	**Trace Element**[‡]	**Concentration mg kg^{-1}**
P	11.5 ±0.02	**As**	0.11 ±0.004
Ca	34.4 ±0.84	**Cr**	0.02 ±0.00
Mg	1.2 ±0.05	**Pb**	0.01 ±0.00
K	0.6 ±0.01	**B**	0.01±0.00
Na	0.2 ±0.01	**Cd**	<DL*
Fe	0.2 ±0.00	**Cu**	<DL
Al	0.2 ±0.00	**Mo**	<DL
S	0.02 ±0.00	**Se**	<DL

[†]Measured using inductively coupled plasma optical emission spectrometer (ICP-OES)
[‡]Measured using inductively coupled plasma mass spectrometer (ICP-MS)
* Below the detection limit of ICP-MS, 0.01 mg kg^{-1}

A powder X-ray Diffraction (XRD) provides insights into crystalline structures and its detection limit is about 2 wt.% of the sample (Klug & Alexander. 1974; Ali et al., 2022). The broader peak between 25° and 35° 2θ position in XRD (Figure 4.1) was similar to the main hydroxyapatite peak (Liu & Lal, 2014). The results indicated the presence hydroxyapatite and the product's amorphous nature by enhanced background and broader peak. The conditions of formation of the recovered products result physical and chemical differences in the products

(Massey et al., 2010). Factors like retention time and complexity of the wastewater matrices could interfere with crystallization process (Stratful et al. 2001; Valsami-Jones, 2001; Le Corre et al., 2005).

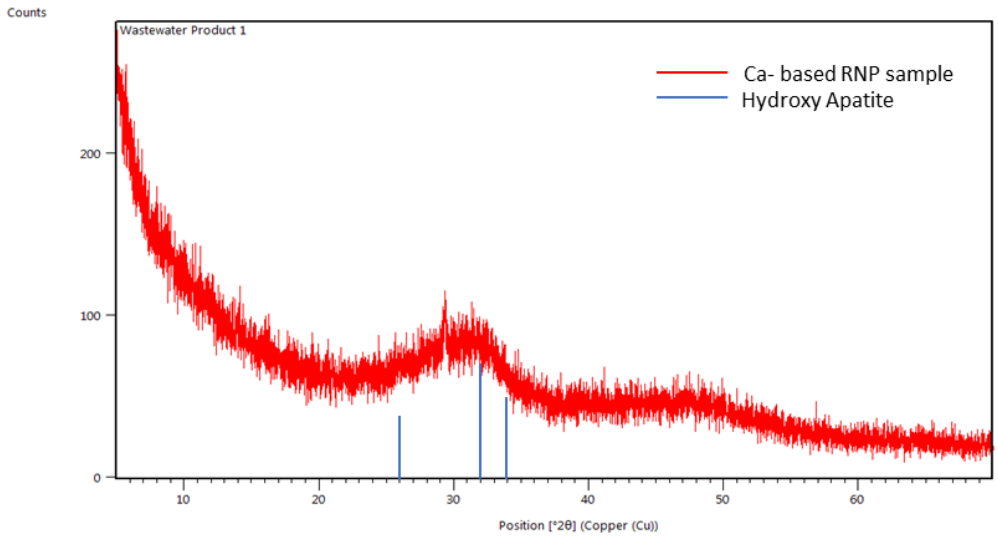


Figure 4.1. The X-ray diffractogram of the recovered nutrient product

Scanning electron microscopy and energy dispersive X-ray analyzer (SEM-EDX) were also used to further characterize the RNP. As shown in an example SEM image in Figure 4.2a, the particles had an irregular shape, and homogeneous nature. The data collected from a selected particle from backscattered electron (BSE) images-energy dispersive X-ray (EDX) (Figure 4.2b, 4.2c) showed the product is rich in Ca and P. Atomic number sensitivity of BSE images can be exploited to distinguish particles with different chemical composition and the EDX allows to get the elemental composition on the surface. Regions of high average atomic number will appear bright relative to regions of low atomic number. The results confirmed the presence of high Ca in the product. X-ray absorption near-edge structure spectroscopy analysis of the RNP (Figure 4.2d) provided further evidence that this product was rich in apatite-like P solid. The XANES results confirmed that the composition of this RNP and residual (minor un-fitted parts) might be a result

of heterogeneous nature of the product and not having a well-defined crystalline structure. Zohar et al., 2018, and Massey et al., 2018 used combined chemical extractions, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), and XANES spectroscopy to quantify speciation in P recovered from wastewater. The P K-edge XANES spectra of recovered dittmarite from cheese processing plant appeared pure and the crystalline struvite materials recovered from dairy wastewater showed 17% apatite and 83% struvite in Massey, 2019. Recovered P availability and uptake of P by crops depend greatly on soil conditions, the type of P fertilizer applied, and specific crop characteristics (Massey et al., 2009; Antonini et al., 2012; Vogel et al., 2017).

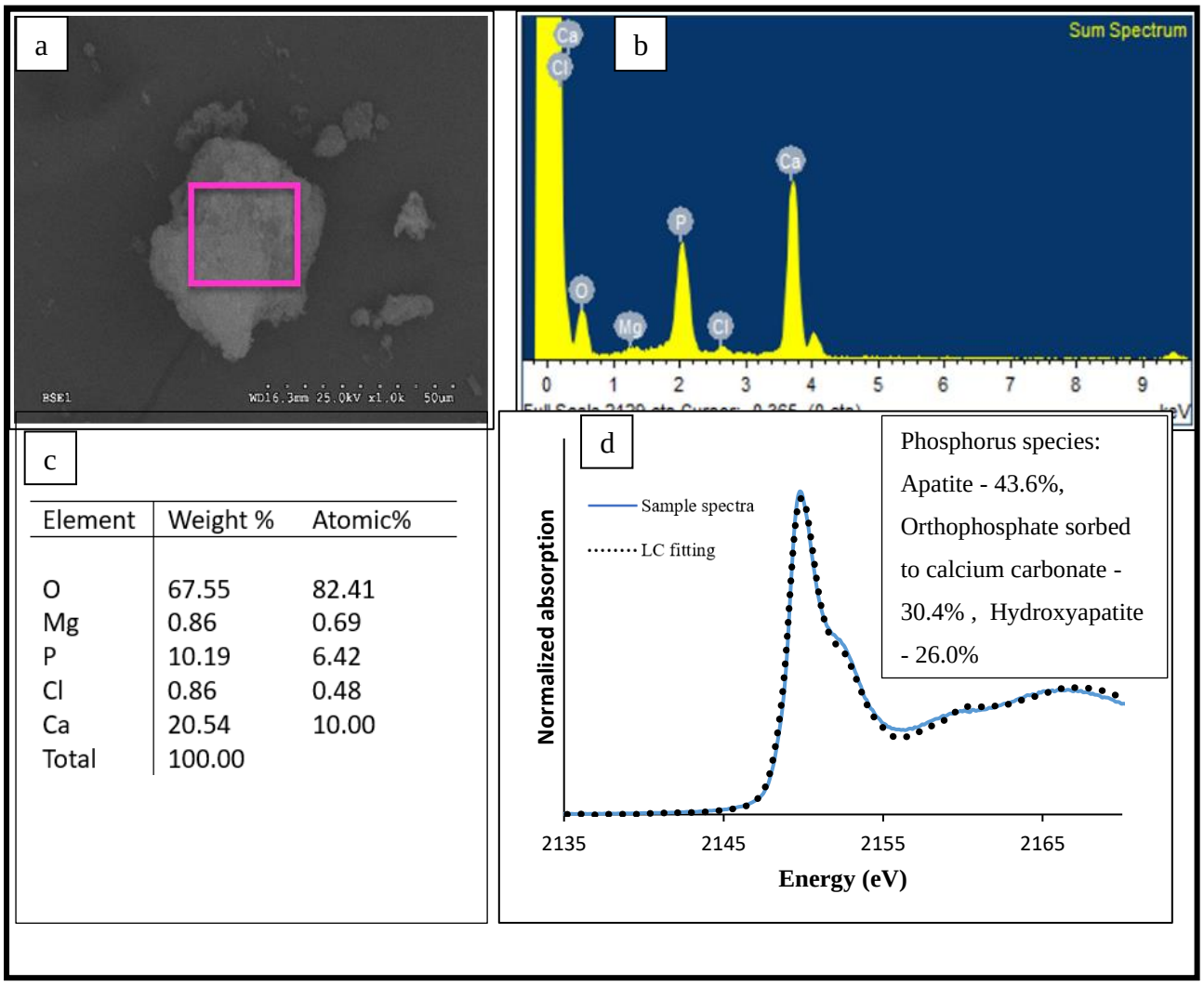


Figure 4.2. (a) Backscattered electron image of the recovered nutrient product (RNP). The area selected to do the elemental composition, is outlined in pink. (b) Elemental composition of the selected area by energy dispersive X-ray spectroscopy (c) Table of elemental composition of the (b). (d) Normalized P K-edge X-ray absorption near edge structure spectra with results of linear combination fitting for the RNP.

Potential plant availability of RNP in soils

Selected physical and chemical properties of the soils used for the incubation studies (Table 4.2), showed that the initial soil pH displayed characteristics of calcareous, neutral, and acidic soils, respectively. Calcareous soil was only mildly calcareous with 7.8% $CaCO_3$.

Table 4.2. Selected physical and chemical properties of the soils used for the incubation study.

Parameter	Value		
	Calcareous soil	**Neutral soil**	**Acidic soil**
pH (1:10 soil:water)	8.7±0.1	7.2±0.1	5.2±0.1
CEC, $cmol_c$/kg	22.1	16.3	2.3
Calcium Carbonate, %	7.8	N/A	N/A
Total P, mg/kg	643.9±4.4	428.5±5.1	14.7±1.2
Available P, mg/kg	37.6 (Olsen P)	79.0 (Mehlich III P)	2.8 (Mehlich III P)
Resin P, mg/kg	62.4±0.2	28.1±0.3	2.3±0.1
Total Organic C, %	1.5	3.32	0.47
Total N, %	0.2	0.28	0.05
Texture	Silt Loam	Silt Loam	Loamy Sand
(Sand, Silt, and Clay %)	(18.4,58.2,23.4)	(9,69,22)	(87,1.5,11.5)

Diffusion of P

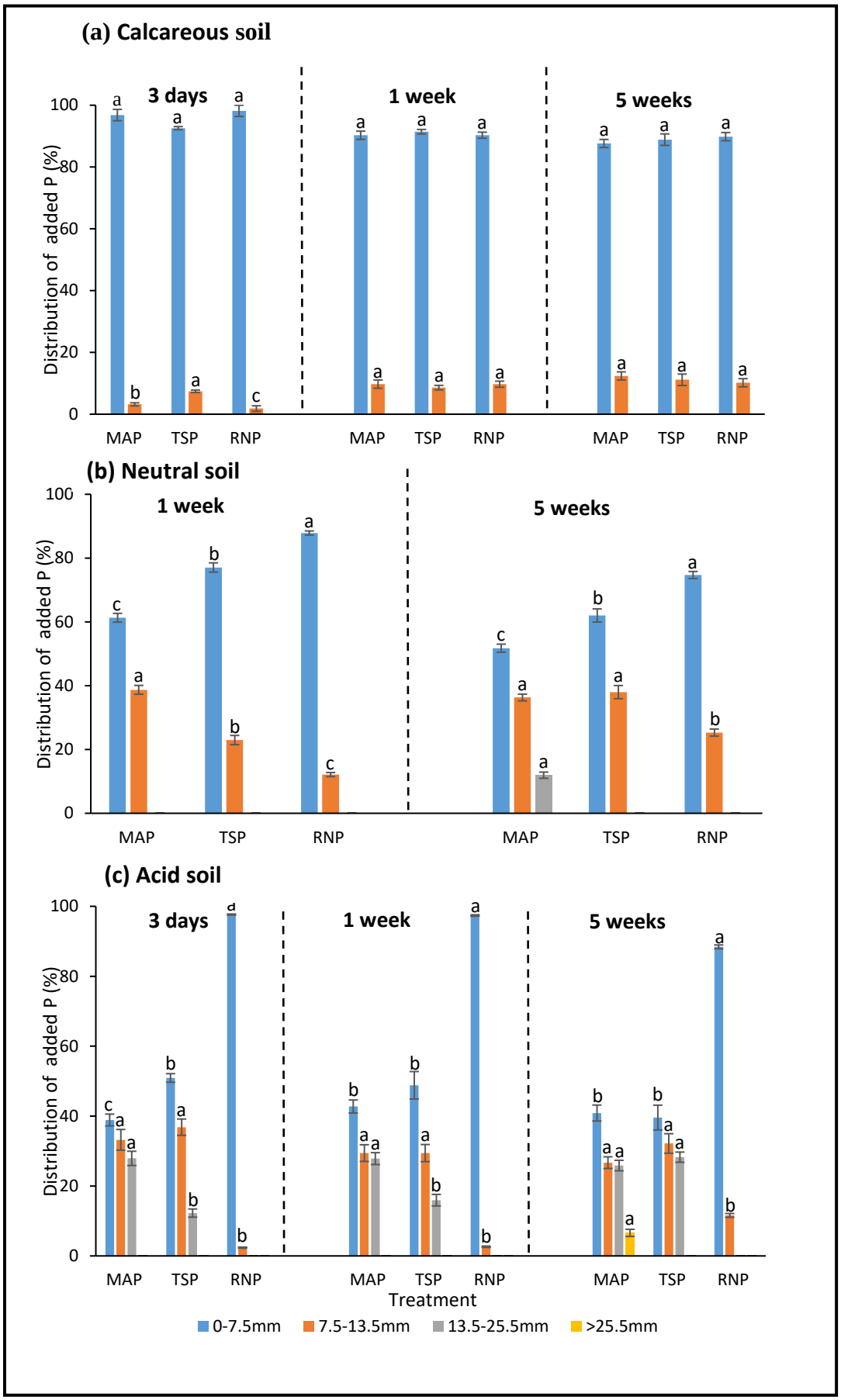

(a) Calcareous soil
3 days
1 week
5 weeks
Distribution of added P (%)
100
80
60
40
20
0
MAP
TSP
RNP
(b) Neutral soil
1 week
5 weeks
(c) Acid soil
3 days
1 week
5 weeks
Treatment
0-7.5mm
7.5-13.5mm
13.5-25.5mm
>25.5mm

Figure 4.3. Distribution of added P (%) after (a) 3 days, 1 week, and 5 weeks of incubation in calcareous soil (b) 1 week and 5 weeks of incubation in neutral soil (c) 3 days, 1 week, and 5 weeks of incubation in acid soil. Means within a soil section for each treatment each time period containing the same letter are not significantly different at $p = 0.05$ according to Tukey's pairwise method.

The P diffusion in calcareous soil showed that most P added remained within the first section for all time durations (Figure 4.3a). Phosphorus diffusion was greater for TSP, followed by MAP, followed by RNP to the second section after 3 days. This could be attributed to the initial acidulation effect of TSP and MAP treatments (Figure 4.4). However, P diffusion in all treatments from the center to the next section was the same at the end of 1 week and the same trend continued till 5 weeks (Figure 4.3a). Limited movement of added nutrients in calcareous soil results from rapid and intense precipitation and sorption reactions with calcium in soil solution, solid calcium carbonates, and other colloids (Lombi et al., 2004; Hettiarachchi et al., 2006; Pierzynski & Hettiarachchi, 2018). Lombi et al., 2004 also reported similar results for the diffusion of MAP applied, as either granular or powdered forms after 5 weeks of incubation. Higher clay and calcium carbonate contents would increase the number of P reactive sites per given soil volume and decrease average solution P concentrations. The decreased solution concentration would reduce the slope of the gradient and potentially slow overall diffusion (Weeks & Hettiarachchi, 2020, Olsen & Watanabe, 1963).

In neutral soil, at the end of 5 weeks, diffusion of TSP and RNP was only from the center to the second section, while MAP diffused from the center to the third section (Figure 4.3b). This could be attributed to the pH reduction in first three sections of MAP added treatment compared to TSP and RNP added treatments (Figure 4.4). In neutral-to-calcareous soils, P retention is dominated by precipitation reactions (Lindsay et al., 1979), although P can also be adsorbed on

the surface of Ca. In neutral soil, three struvites showed much less P diffusion than the treatment MAP in a petri dish diffusion experiment conducted by Degryse et al., 2017.

In acid soil at the end of 5 weeks, a significant portion of MAP and TSP (~60%) was moved away from the center section where diffusion of RNP was significantly less and diffused less further (only from the center to the second section, Figure 4.3c). Even after 5 weeks,> 80% of RNP was retained in the center section. In acid soils, surface sorption and precipitation reactions with Fe and Al reduce the overall P diffusion (Sample et al., 1980). However, the soil texture might influence the enhanced diffusion in this acid soil compared to the other two soils. Acid soil was a loamy sand, while the other two soils were silt loam. The loamy sand texture could lead to better diffusion of P in soil. Olsen & Watanabe, 1963 observed that the Oxisol's clay soil texture contributed to reduced P movement from the center section. The diffusion of MAP is superior in both neutral and acid soils from the beginning compared to the TSP. In TSP, quick saturation of the adsorption sites is possible, and after this initial phase, adsorption reactions limit further movement. This is discussed further in the section of P reaction products.

Potential plant available P and pH

Plant availability of P can be determined directly through plant uptake studies and indirectly through different extraction procedures. Labile P in soil appears to be isotopically exchangeable or anion resin extractable. The resin-extractable P method mimics the soil/soil solution/plant root model (Myers et al., 2005). The indirect resin-extractable P method is superior to most common extraction procedures such as Olsen P, Bray 1-P, and Mehlich P for determining plant available P (Saggar et al., 1990).

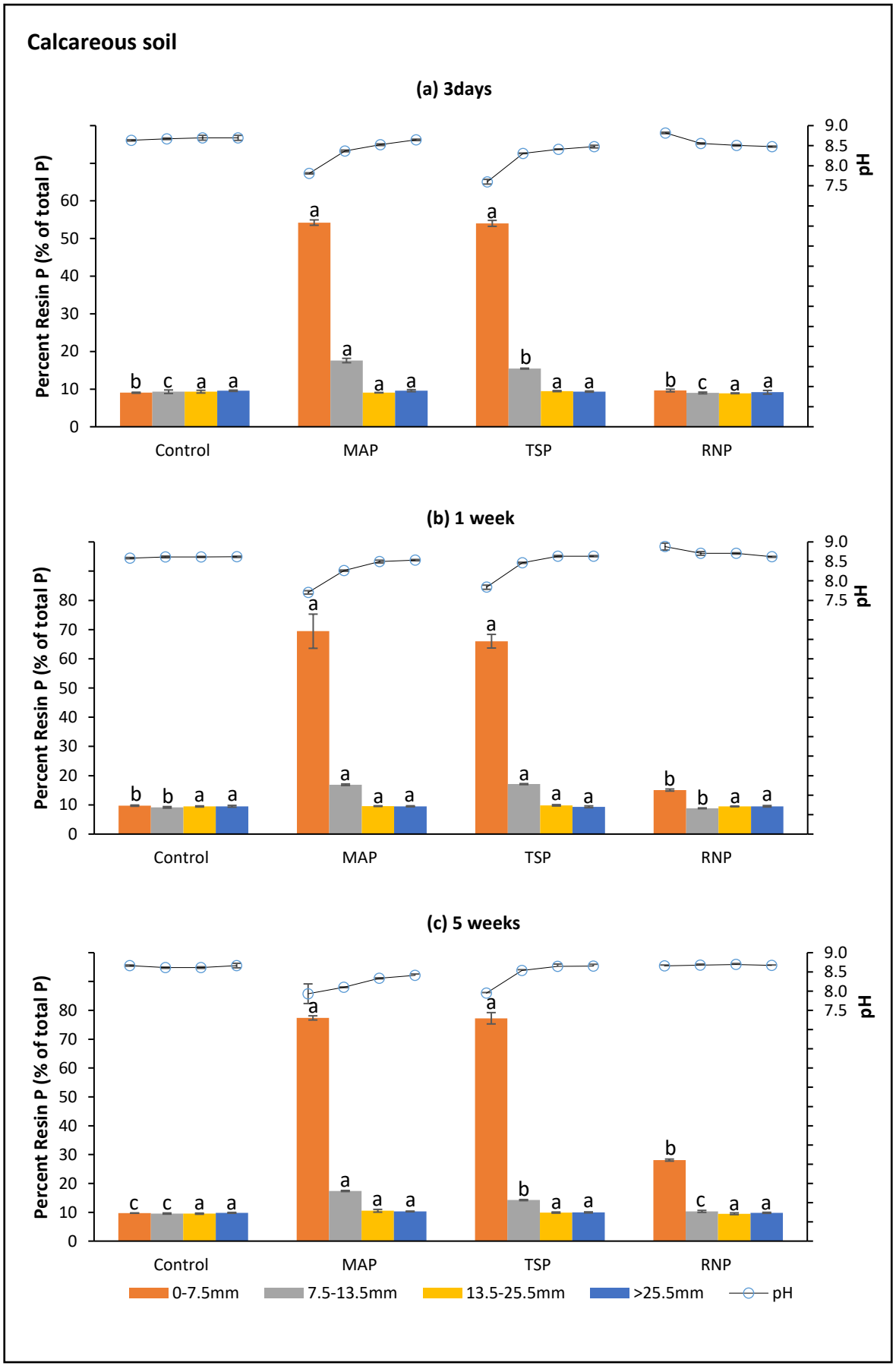

Calcareous soil
(a) 3days
Percent Resin P (% of total P)
pH
Control
MAP
TSP
RNP
(b) 1 week
(c) 5 weeks
0-7.5mm
7.5-13.5mm
13.5-25.5mm
>25.5mm
pH

Figure 4.4. Percent resin P (PRP) and the pH for each dish section for all treatments after (a) 3 days, (b) 1 week and (c) 5 weeks of incubation in calcareous soil. Means within a soil section for each treatment containing the same letter are not significantly different at p = 0.05 according to Tukey's pairwise method.

In calcareous soil after 3 days of incubation, the highest availability of percent resin P (PRP) was in the center section of MAP and TSP added treatments, whereas the center section of RNP showed similar PRP availability to control (Figure 4.4a). However, with time P availability in the center section of RNP increased and showed a higher availability of PRP than the control after 1 week (Figure 4.4b) and the same trend continued through 5 weeks (Figure 4.4c). The maximum reduction of pH was observed in the center section of MAP and TSP. As mentioned above, phosphate adsorption and precipitation reactions with calcium carbonate determine the P availability in calcareous soils. Carbonate content, different Ca:P ratios, and pH at the moment of precipitation would impact the type of Ca-P that forms, mineral crystallinity, and thus stability determining solubility (Baig et al., 1999; Raynaud et al., 2002; Wang & Nancollas, 2008; Lei et al., 2017; Weeks & Hettiarachchi, 2020). The fertilizer MAP contains ammonium N. Nitrification of ammonium-N contained within the P fertilizers results in acidification (Hanson & Westfall, 1985). This reaction is limited by the overall buffering capacity of the soil carbonates (Lombi et al., 2004; Hettiarachchi et al., 2010). Due to the indirect nature of soil acidification by MAP, it could persist longer than TSP. According to Lindsay, 1979, the dissolution of TSP causes direct soil acidification. Triple superphosphate, which contains monocalcium phosphate [$Ca(H_2PO_4)_2 \cdot H_2O$], dissociates H^+ ions from the $H_2PO_4^-$ molecule and generates acidity. The pH reduction results in greater solubility and, therefore, greater P availability. The RNP buffered the soil pH around the original soil pH (8.7) even after 5 weeks of application. The presence of excess Ca salts added during the production process could lead to suppression of dissolution of RNP, whose speciation is also dominated by Ca-P. This is supported by the slightly enhanced pH

observed in the RNP center section at 3-days (Figure 4.4a). Degryse et al., 2017 also showed that excess base in the waste recovered struvite reduced its dissolution rate in soil, and it depends on the soil properties such as pH buffering capacity.

In neutral soil, the center section of MAP and TSP added treatments showed the highest PRP, followed by the center section of RNP added treatment after 5 weeks (Figure 4.5b). Although ~ 12 to 39% of P diffused into the second section by one week, the PRP in the second section for any treatment was not significantly different from the control (Figure 4.5a), suggesting strong P sorption. Phosphorus is adsorbed on the surfaces of clay, amorphous Al or Fe oxides in acid soils, and calcium carbonate in alkaline soils. According to Sposito, 1989, most adsorbed P in soil occurs as inner-sphere complex species (specific adsorption), and some P is adsorbed as either diffuse ion swarm or outer-sphere complex species (nonspecific adsorption). Inner-sphere complex P is slower to equilibrate with the soil solution P than the outer sphere and diffuse swarm P (Khatiwada et al., 2012). Recovered nutrient products buffered the soil pH in the center section around 7.8, RNP's original pH, which is higher than the control soil pH after 5 weeks of incubation. The high pH of RNP was due to the excess Ca salts added during the production process. However, the availability of the P from the RNP in the center section was higher than the control.

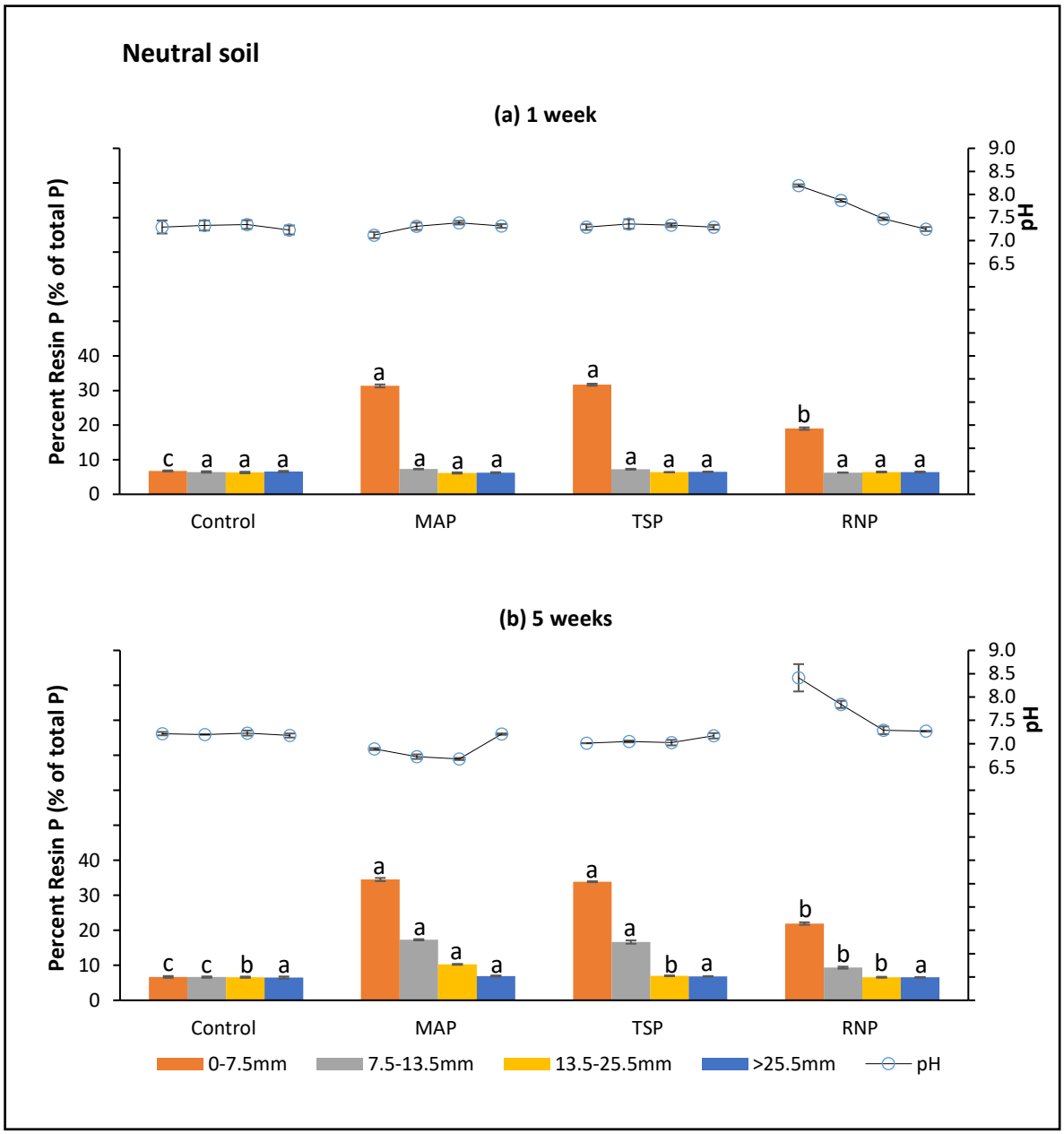


Figure 4.5. Percent resin P (PRP) and the pH for each dish section for all treatments after (a)1 week and (b) 5 weeks of incubation in neutral soil. Means within a soil section for each treatment containing the same letter are not significantly different at p = 0.05 according to Tukey's pairwise method.

In the acid soil, the center section of MAP and TSP added treatments showed the highest PRP than the RNP added treatment after 3 days and 1 week (Figure 4.6a, 4.6b). However, at the end of 5 weeks, the PRP was similar in the center sections of MAP and RNP added treatments (Figure 4.6c). The less resin extractability in the center section of MAP treatment over time due to saturation of the adsorption sites. Decrease extractability indicates either change in the adsorption mechanism (outer sphere change into an inner sphere) or a change in the crystallinity of precipitates. In MAP treatment pH further decreased over time which could facilitate the process. In contrast, the diffusion for the RNP treatments was slower and proceeded more gradually, which can be explained by the ongoing dissolution of the RNP. Degryse et al., 2017 observed similar results for MAP and struvite using the P diffusion visualization technique. The lower PRP values observed in this acid soil are consistent with other studies that demonstrate P applied to soils containing varying amounts of Fe and Al oxide materials may be subject to sorption reactions that significantly reduce the overall P extractability (Parfitt et al., 1989; Hedley & McLaughlin, 2005; Kizewski et al., 2011). In addition, the acidic pH of the soils may have contributed to the solubilization of Fe and Al, thus the precipitation with fertilizer P (Hesterberg, 2010; Hedley & McLaughlin, 2005).

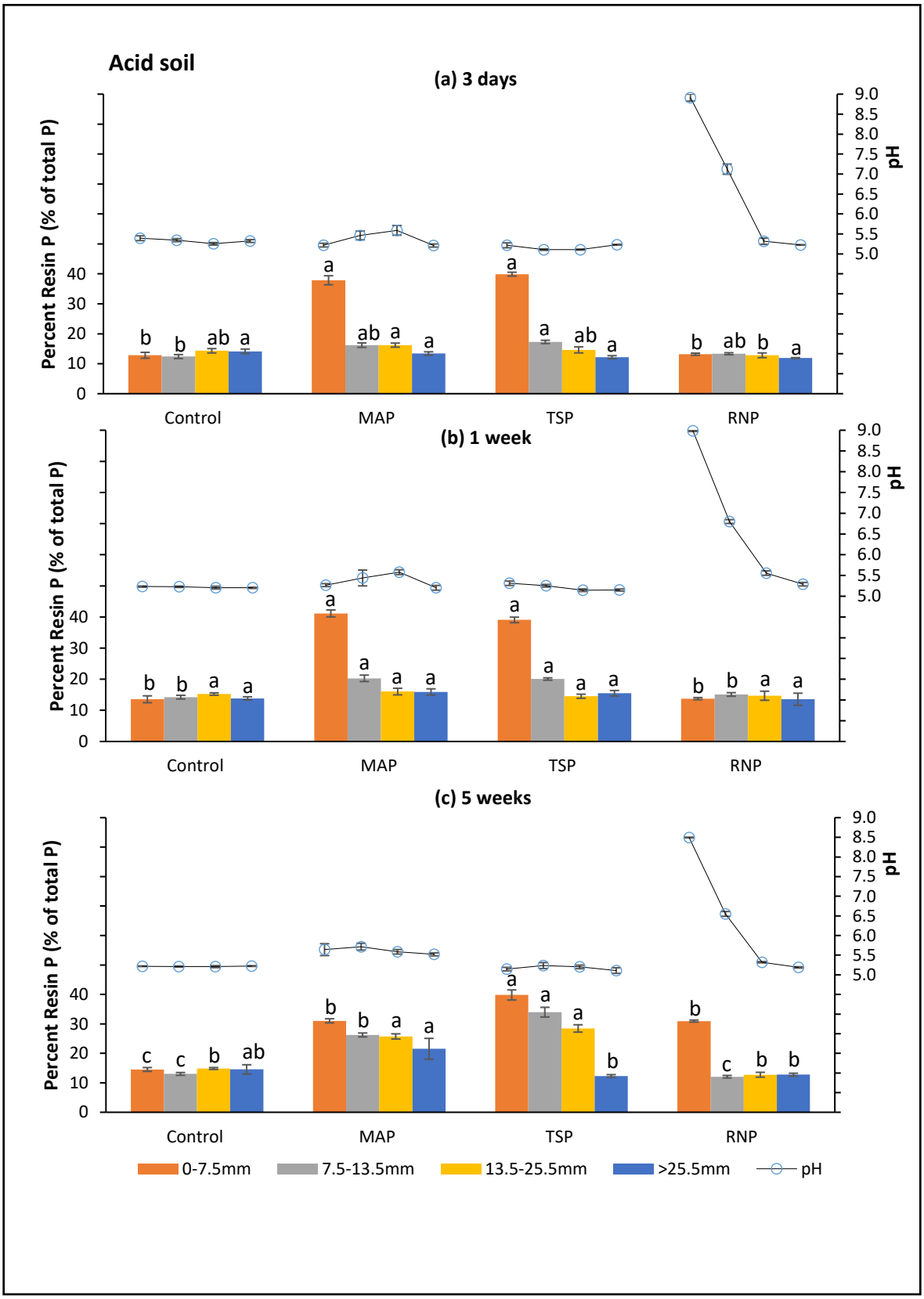

Acid soil
(a) 3 days
(b) 1 week
(c) 5 weeks
Percent Resin P (% of total P)
pH
Control
MAP
TSP
RNP
0-7.5mm
7.5-13.5mm
13.5-25.5mm
>25.5mm
pH

Figure 4.6. Percent resin P (PRP) and the pH for each dish section for all treatments after (a) 3days, (b) 1 week and (c) 5 weeks of incubation in acid soil. Means within a soil section for each treatment containing the same letter are not significantly different at $p = 0.05$ according to Tukey's pairwise method.

Reaction products of P

The XANES technique allows the determination of the oxidation state and an element's local chemical and structural environment (Fendorf & Sparks, 1996), enabling speciation. The speciation of contaminants and nutrients in soils significantly determines their availability and fate in the environment. This technique has been widely used for the speciation of organic and inorganic P in soils, sediments, agricultural byproducts and fertilized soils (Hesterberg et al., 1999; Peak et al., 2002; Beauchemin et al., 2003; Khatiwada et al., 2012; Lombi et al., 2011; Ajiboye et al., 2008; Kruse & Leinweber, 2008; Weeks & Hettiarachchi, 2020).

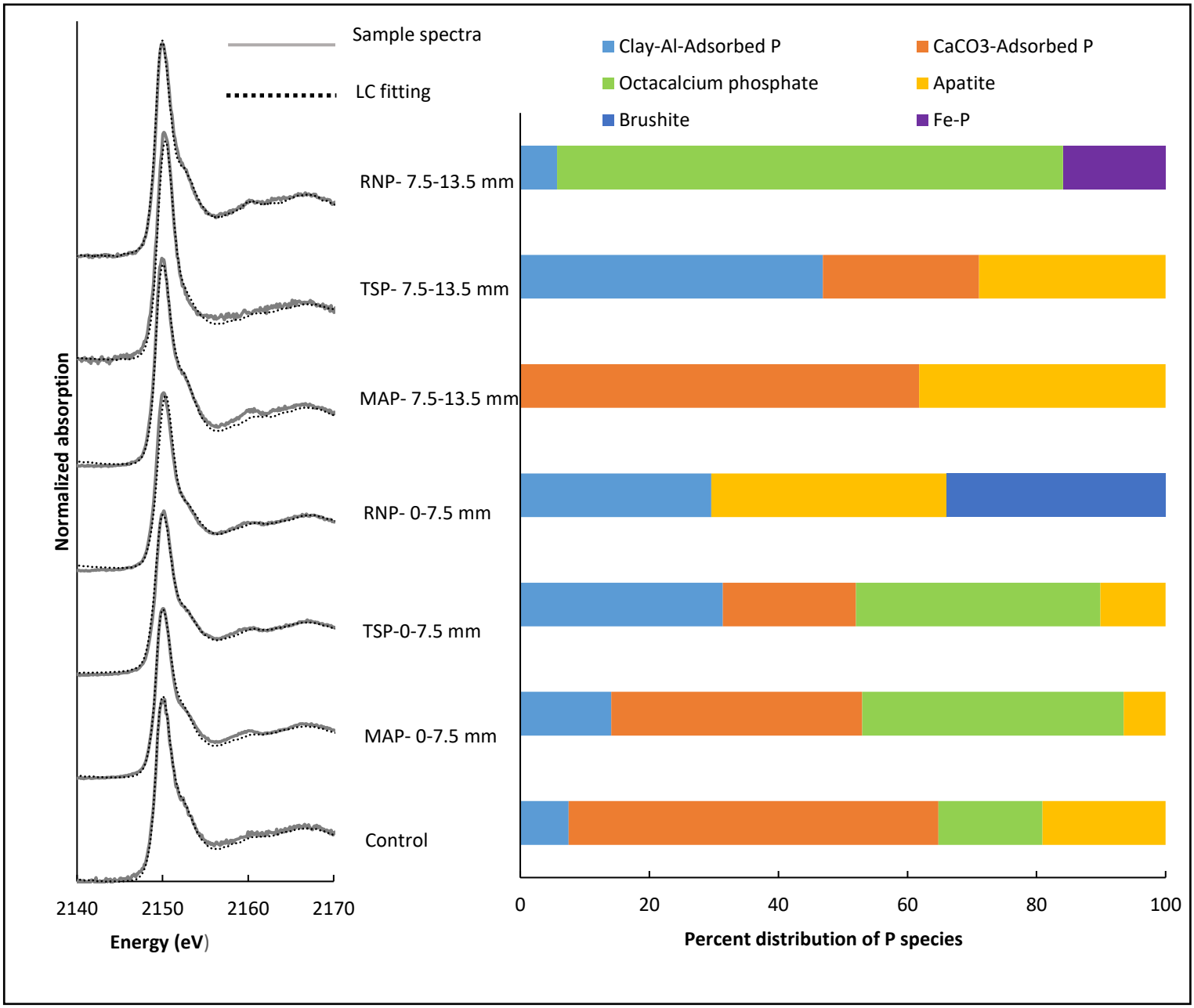


Figure 4.7. Normalized P K-edge X-ray absorption near edge structure spectra of selected dish sections with results of linear combination fitting as percent distribution of P species in calcareous soil. MAP, monoammonium phosphate; TSP, triple superphosphate; RNP, recovered nutrient product; Clay-Al-P - Aluminum bridged phosphate sorbed to montmorillonite; Fe-P- Iron precipitated P.

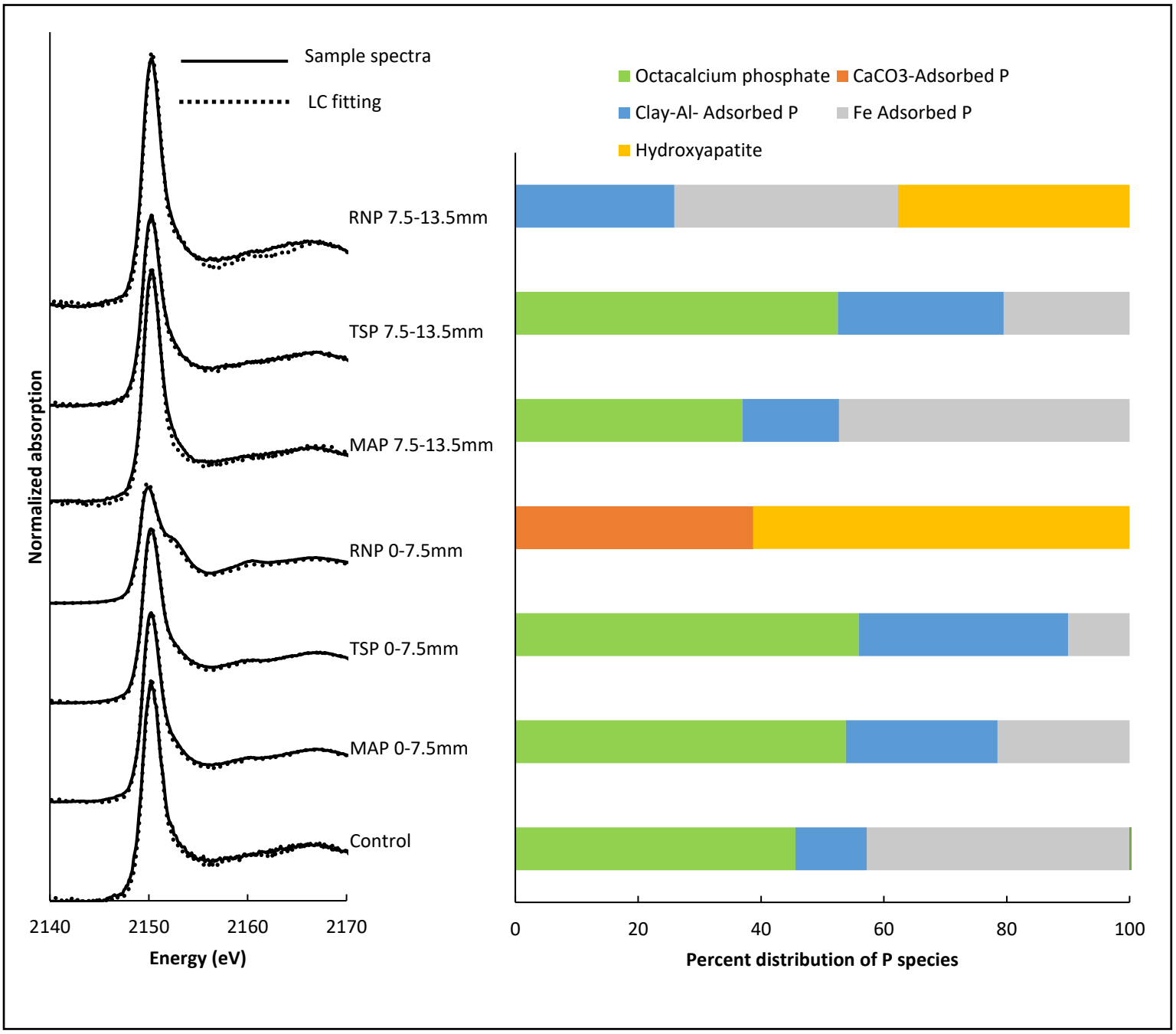


Figure 4.8. Normalized P K-edge X-ray absorption near edge structure spectra of selected dish sections with results of linear combination fitting as percent distribution of P species in neutral soil. MAP, monoammonium phosphate; TSP, triple superphosphate; RNP, recovered nutrient product; Clay-Al-P - Aluminum bridged phosphate sorbed to montmorillonite.

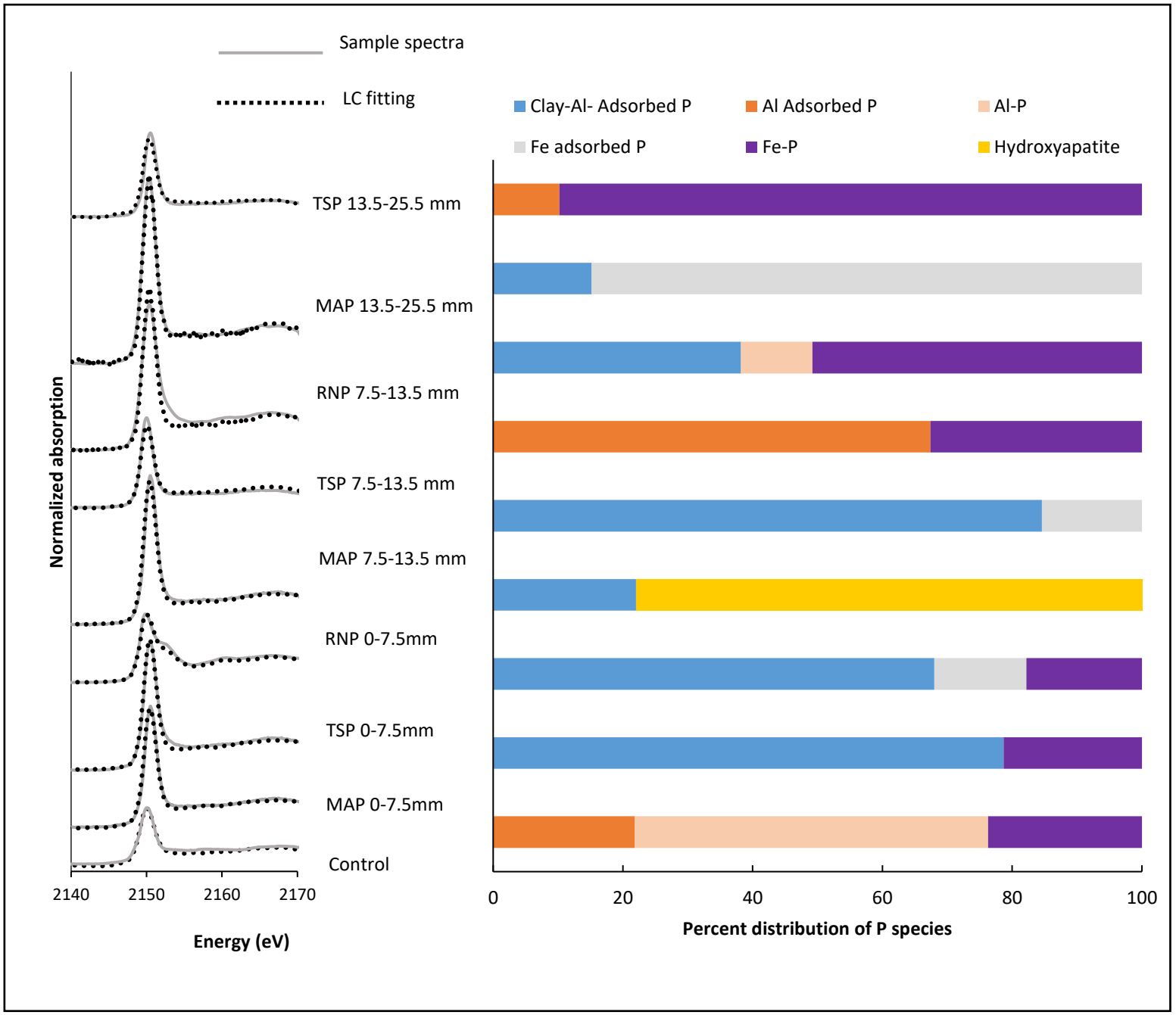


Figure 4.9. Normalized P K-edge X-ray absorption near edge structure spectra of selected dish sections with results of linear combination fitting as percent distribution of P species in acid soil. MAP, monoammonium phosphate; TSP, triple superphosphate; RNP, recovered nutrient product; Clay-Al-P - Aluminum bridged phosphate sorbed to montmorillonite.

In calcareous soil, nonfertilized control treatment was dominated by $CaCO_3$ adsorbed P (Figure 4.7). The MAP and TSP center sections confirm that most P was associated with Ca as sorbed to $CaCO_3$ or OCP (Figure 4.7). As expected from the resin extractable results, RNP added treatment center section was dominated by more insoluble precipitated species like apatite, which could be the reason for reduced solubility. In the neutral soil, the nonfertilized control treatment was dominated by OCP and $CaCO_3$ adsorbed P species (Figure 4.8). The center sections of MAP and TSP also showed the majority of P in OCP and the rest in $CaCO_3$ or clay-adsorbed P. In the neutral soil, the RNP-added treatment center section was still dominated by more insoluble precipitated species like hydroxyapatite. The unfertilized control treatment in acid soil contained P mainly as Al-P and Fe-P precipitates and Fe- and Al-adsorbed P (Figure 4.9). Adding the MAP and TSP fertilizer resulted in clay-adsorbed species, whereas RNP was dominated by less soluble hydroxyapatite in the center dish section. It seems that alkaline pH of RNP is restricting its solubility (mobility) and resin extractability. Speciation of P in all soils treated with RNP (where we have remaining RNP- not dissolved and moved) indicated that speciation did not change much in any of the soils likely due to its original speciation combined with residual alkalinity. The increased adsorbed species for both MAP and TSP treatments may be the reason for the increased PRP in the center dish section compared to RNP. Khatiwada et al., 2012 conducted a field study with reduced tillage to study P availability at various distances from either deep-banded or broadcast MAP P fertilizers and technical grade monoammonium P added in liquid form and the reaction products formed within a Mollisol. Comparison of resin-extractable P data with speciation results showed a positive correlation of adsorbed P species with resin-extractable P, suggesting that adsorbed P species might be more available. In acidic Oxisols, Fe and Al metal oxide or oxyhydroxide surfaces have a strong capacity to adsorb P, and therefore the prevalence of the adsorbed species was not unexpected. Pierzynski &

Hettiarachchi, 2018 also observed that added fertilizer P transformed into Fe-adsorbed P, Fe-P, and Al-P in 5 weeks incubation study in an oxisol. Iron phosphates are known to control the solubility of P under acidic conditions (Lindsay, 1979). Parfitt, 1989 found that in acidic soils, the reactions of P sorption involved hematite, goethite, ferrihydrite, and allophane minerals.

Summary

The findings of this study showed that RNP acted as a P source for all three tested soils. The P diffusion and percent resin extractable P results demonstrated that RNP had less performance than conventional fertilizers (MAP and TSP). The P speciation in both RNP and RNP added soils showed that the speciation was dominated by the less soluble apatite and hydroxyapatite like species which explains the reduced solubility and extractability of RNP in the tested soils. The low solubility and the slow release of P in RNP are helpful in specific agricultural production systems. While the results are promising, identifying the P content of potential fertilizers and understanding P speciation and behavior of the recovered products in different soils are essential to implement P recovery from waste streams and beneficial reuse of P in agricultural production. However, physical and chemical heterogeneity may lead to differences in the fertilizer value of the recovered products. Modified AnMBR process could lead to RNPs with higher total P% and more solubility. Optimizing Ca-based RNP recovery may offer useful secondary P sources in agriculture. Further research is needed to improve removal efficiency and regularity of precipitate characteristics using actual wastewater under field conditions.

References

Achat, D.L., M. Sperandio, M. L. Daumer, A.C. Santellani, L. Prud'Homme, M. Akhtar, and C. Morel. 2014. Plant-availability of phosphorus recycled from pig manures and dairy effluents as assessed by isotopic labeling techniques. Geoderma. 232–234: 24–33.

Ajiboye, B., O.O. Akinremi, Y. Hu and A. Jurgensen. 2008. XANES speciation of phosphorus in organically amended and fertilized Vertisol and Mollisol. Soil Sci. Soc. Am. J. 72:1256-1262.

Ali, A., Y. W. Chiang, and R.M. Santos. 2022. X-ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions. Minerals. 12: 205. https://doi.org/10.3390/min12020205

Allison, L. and C. Moodie. 1965. Carbonate. Cation-exchange capacity. *In* A.G. Norman (ed.) Methods of Soil Analysis. Part-2. Chemical and Microbiological Properties. SSSA, Madison, WI.

Antonini, S., M.A. Arias, T. Eichert, and J. Clemens. 2012. Greenhouse evaluation and environmental impact of different urine-derived struvite fertilizers as phosphorus sources for plants. Chemosphere. 89: 1202-1210.

Association of Official Analytical Chemists, 1945. H.A. Lepper. Official methods of analysis.

Baig, A.A., J.L. Fox, R.A. Young, Z. Wang, J. Hsu, W.I. Higuchi, A. Chhettry, H. Zhuang, and M. Otsuka. 1999. Relationships among carbonated apatite solubility, crystallite size, and microstrain parameters. Calcif. Tissue Int. 64: 437-449.

Beauchemin, S., D. Hesterberg, J. Chou, M. Beauchemin, R.R. Simard and D.E. Sayers. 2003. Speciation of phosphorus in phosphorus-enriched agricultural soils using x-ray absorption near-edge structure spectroscopy and chemical fractionation. J. Environ. Qual. 32: 1809–1819.

Braithwaite, A., and P. Eaton. 1990. Groom Factors affecting the solubility of phosphate rock residues in 2% citric acid and 2% formic acid. Fertilizer research. 23(1): 37-42.

Brod, E., A. F. Øgaard, E. Hansen, D. Wragg, T. K. Haraldsen, and T. Krogstad. 2015a. Waste products as alternative phosphorus fertilisers part I: inorganic P species affect fertilisation effects depending on soil pH. Nutr. Cycl. Agroecosys. 103: 167–185.

Cheng, H.-H., B. Narindri, H. Chu, and L.M. Whang. 2020. Recent advancement on biological technologies and strategies for resource recovery from swine wastewater. Bioresour. Technol. 303: 122861–122861. https://doi.org/10.1016/j.biortech.2020.122861

Christiansen, N.H., P. Sørensen, R. Labouriau, B.T. Christensen, and G.H. Rubæk. 2020. Characterizing phosphorus availability in waste products by chemical extractions and plant uptake. J. Soil Sci. Plant Nutr. 183(4): 416-428.

Cordell, D. and S. White. 2013. Sustainable Phosphorus Measures: Strategies and Technologies for Achieving Phosphorus Security. Agronomy. 3(1): 86–116. https://doi.org/10.3390/agronomy3010086

Cordell, D., A. Rosemarin, J. Schröder, and A. Smit. 2011. Towards Global Phosphorus Security: A Systems Framework for Phosphorus Recovery and Reuse Options. Chemosphere. 84(6): 747-758.

Cunha, J. R., C. Schott, R. D. Van der Weijden, L.H. Leal, G. Zeeman, and C. Buisman, 2020. Calcium phosphate granules recovered from black water treatment: A sustainable substitute for mined phosphorus in soil fertilization. Resour Conserv Recycl. 158: 104791. https://doi.org/10.1016/j.resconrec.2020.104791.

Degryse, F., R. Baird, R.C. da Silva, and M.J. McLaughlin. 2017. Dissolution rate and agronomic effectiveness of struvite fertilizers – effect of soil pH, granulation and base excess. Plant Soil. 410: 139-152.

Fendorf, S.E., and D.L. Sparks.1996. X-ray absorption fine structure. p 378-416. *In* D.L. Sparks (ed.) Methods of soil analysis. Part. 3. SSSA, Madison, WI.

Frank, K., D. Beegle, and J. Denning. 1998. Phosphorus. In: J.R. Brown, editor, Recommended chemical soil test procedures for the north central region. Missouri Agric. Exp. Stn. University of Missouri, Columbia, MO. 21–30.

Hanson, R.L., and D.G. Westfall. 1985. Orthophosphate solubility transformations and availability from dual applied nitrogen andphosphorus. Soil Sci. Soc. Am. J. 49: 1283–1289.

Hedley, M., and M. McLaughlin. 2005. Reactions of phosphate fertilizers and by-products in soils. In: J.T. Sims and A. Sharpley, editors, Phosphorus: Agriculture and the environment. Agron. Monogr. 46. ASA, CSSA, and SSSA, Madison, WI. 181–252.

Henze, M., M. C.M. van Loosdrecht, G. A. Ekama, and D. Brdjanovic. 2008. Biological Wastewater Treatment: Principles, Modelling and Design. IWA Publishing.

Heronemus. E. 2021. Phosphorus recovery from anaerobic membrane bioreactor (AnMBR) permeate by chemical coagulation and bioelectrochemical processes. Thesis. Kansas State University, Manhattan, Kansas.

Hesterberg, D. 2010. Macroscale chemical properties and X-ray absorption spectroscopy of soil phosphorus. In: B. Singh and M. Grafe, editors, Synchrotron-based techniques in soils and sediments. Developments in soil science. Elsevier, Burlington, MA. 313–356.

Hesterberg, D., W.Q. Zhou, K.J. Hutchison, S. Beauchemin, and D.E. Sayers. 1999, XAFS study of adsorbed and mineral forms of phosphate. J. Synchrotron Radiat. 6: 636-638.

Hettiarachchi, G.M., E. Lombi, M. McLaughlin, D. Chittleborough, and C. Johnston. 2010. Chemical behavior of fluid and granular Mn and Zn fertilisers in alkaline soils. Soil Res. 48: 238–247.

Hettiarachchi, G.M., E. Lombi, M.J. McLaughlin, D. Chittleborough, and P. Self. 2006. Density changes around phosphorus granules and fluid bands in a calcareous soil. Soil Sci. Soc. Am. J. 70: 960-966.

Huang, H., Xiao, D., Liu, J., Hou, L., & Ding, L. 2015. Recovery and removal of nutrients from swine wastewater by using a novel integrated reactor for struvite decomposition and recycling. Sci. Rep. 5(1): 10183. https://doi.org/10.1038/srep10183

Jenkinson, D., and D. Powlson. 1976. The effects of biocidal treatments on metabolism in soil-V: A method for measuring soil biomass. Soil Biol. Biochem. 8:209–213.

Johnston, A. E., and I. R. Richards. 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. Soil Use Manage. 19: 45–49.

Khatiwada, R., G.M. Hettiarachchi, D. Mengel, and M. Fei. 2012. Speciation of Phosphorus in a Fertilized Reduced Till Soil System: In-Field Treatment Incubation Study. Soil Sci. Soc. Am. J. 76: 2006-2018.

Kilmer, V.J., and L.T. Alexander. 1949. Methods of making mechanical analyses of soils. Soil Sci. 68: 15–24.

Kizewski, F., Y.T. Liu, A. Morris, and D. Hesterberg. 2011. Spectroscopic approaches for phosphorus speciation in soils and other environmental systems. J. Environ. Qual. 40:751–766.

Klug, H.P. and Alexander, L.E. 1974. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. John Wiley & Sons, New York.

Kruse, J., and P. Leinweber. 2008. Phosphorus in sequentially extracted fen peat soils: A K-edge X-ray absorption near-edge structure (XANES) spectroscopy study. J. Plant Nutr. and Soil Sci. 171: 613-620.

Le Corre, K.S., E. Valsami-Jones, P. Hobbs, and S. A. Parsons. 2005. Impact of calcium on struvite crystal size, shape, and purity. J. Cryst. Growth. 283: 514–522.

Lei, Y., B. Song, R. D. van der Weijden, M. Saakes, and C. J. N. Buisman. 2017. Electrochemical Induced Calcium Phosphate Precipitation: Importance of Local pH. Environ. Sci. Technol. 51(19): 11156–11164. https://doi.org/10.1021/acs.est.7b03909

Li, X.Z., and Q. L. Zhao, 2003. Recovery of ammonium–nitrogen from landfill leachate as a multi-nutrient fertilizer. Ecol. Eng. 20: 171–181.

Liao, B.Q., J. T. Kraemer and D. M. Bagley. 2006. Anaerobic Membrane Bioreactors: Applications and Research Directions. Crit Rev Environ Sci Technol. 36: 489–530.

Lim, K., P.J. Evans, and P. Parameswaran. 2019. Long-term performance of a pilot-scale gas-sparged anaerobic membrane bioreactor under ambient temperatures for holistic wastewater treatment. Environ. Sci. Technol. 53: 7347−7354.

Lin, H., W. Peng, M. Zhang, J. Chen, H. Hong and Y. Zhang. 2013. A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives. Desalination. 314: 169–188.

Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Liu, R., and R. Lal. 2014. Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (*Glycine max*). Sci Rep. 4: 5686. https://doi.org/10.1038/srep05686

Lombi E., G. M. Hettiarachchi, and K. G. Scheckel. 2011. Advanced in situ spectroscopic techniques and their applications in environmental biogeochemistry: Introduction to the special section. J. Environ. Qual. 40: 659-666.

Lombi, E., M. J. McLaughlin, C. Johnston, R.D. Armstrong, and R.E. Holloway. 2004. Mobility and lability of phosphorus from granular and fluid monoammonium phosphate differs in a calcareous soil. Soil Sci. Soc. Am. J. 68: 682-689.

Massey M.S., J. A. Ippolito, J. G. Davis, R. E. Sheffield. 2010. Macroscopic and microscopic variation in recovered magnesium phosphate materials: Implications for phosphorus removal processes and product re-use. Bioresour. Technol. 101: 877–885.

Massey, M., J. Davis, J. Ippolito, and R. Sheffield. 2009. Effectiveness of recovered magnesium phosphates as fertilizers in neutral and slightly alkaline soils. Agron. J. 101: 323–329.

Massey, M.S., 2019. X-ray spectroscopic quantification of Struvite and Dittmarite recovered from wastewater. J. Environ. Qual. 48: 193–198.

Massey, M.S., I. Zohar, J.A. Ippolito, and M.I. Litaor. 2018. Phosphorus sorption to aluminum based water treatment residuals reacted with dairy wastewater: 2. X-ray Absorption Spectroscopy. J. Environ. Qual. 47: 546–553.

Meinen, R. J., K. B. Kephart, and R.E. Graves. 2014. Economic feasibility and evaluation of a novel manure collection and anaerobic digestion system at a commercial swine finisher enterprise. Biomass Bioenergy. 63: 10–21. https://doi.org/10.1016/j.biombioe.2014.01.032

Moody, P. W. 2011. Environmental risk indicators for soil phosphorus status. Soil Res. 49: 247-252.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27: 31-36.

Myers, R.G., A.N. Sharpley, S.J. Thien, and G.M. Pierzynski. 2005. Ion-sink phosphorus extraction methods applied on 24 soils from the continental USA. Soil Sci. Soc. Am. J. 69: 511-521.

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. In: D.L. Sparks, A. Page, P. Helmke, R. Loeppert, P. Soltanpour, M. Tabatabai, et al., editors, Methods of soil analysis. Part 3. Chemical methods. ASA, CSSA, SSSA, Madison, WI.

Olsen, S.R. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. Issue 939 of Circular United States. Department of Agriculture.

Olsen, S.R., and F.S. Watanabe. 1963. Diffusion of phosphorus as related to soil texture and plant uptake. Soil Sci. Soc. Am. J. 27: 648–653.

Parfitt, R.L., L.J. Hume, and G.P. Sparling. 1989. Loss of availability of phosphate in New Zealand soils. J. Soil Sci. 40: 371–382.

Pierzynski, J. and G. M. Hettiarachchi. 2018. Reactions of phosphorus fertilizers with and without a fertilizer enhancer in three acidic soils with high phosphorus-fixing capacity. Soil Sci. Soc. Am. J. 82: 1124-1139.

Raby, K., A. Avalos Ramirez, and M. Heitz. 2013. Elimination of nitrogen present in swine manure using a high-efficiency biotrickling filter. Environ. Technol. 34(7): 813–824. https://doi.org/10.1080/09593330.2012.720615

Ravel B., and M. Newville. 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12: 537–541.

Raynaud, S., E. Champion, D. Bernache-Assollant, and P. Thomas. 2002. Calcium phosphate apatites with variable Ca/P atomic ratio I. synthesis, characterization, and thermal stability of powders. Biomaterials. 23: 1065-1072.

Rech, I., P. Withers, D. Jones, P. Pavinato. 2018. Solubility, diffusion and crop uptake of phosphorus in three different struvites. Sustainability 11(1): 134.

Robles, Á., D. Aguado, R. Barat, L. Borrás, A. Bouzas, J. B. Giménez, N. Martí, J. Ribes, M. V. Ruano, J. Serralta, J. Ferrer, and A. Seco. 2020. New frontiers from removal to recycling of nitrogen and phosphorus from wastewater in the Circular Economy. Bioresour. Technol. 300: 122673-122673.

Roychand, R., B. Kumar Pramanik, G. Zhang, and S. Setunge. 2020. Recycling steel slag from municipal wastewater treatment plants into concrete applications – A step towards circular economy. Resour Conserv Recycl. 152: 104533. https://doi.org/10.1016/j.resconrec.2019.104533

Saggar, S., M.J. Hedley, and R.E. White. 1990. A simplified resin membrane technique for extracting phosphorus from soils. Fert. Res. 24: 173–180.

Sample, E., R. Soper, and G. Racz. 1980. Reactions of phosphate fertilizers in soils. In: F.E. Khasawneh, E.C. Sample, and E.J. Kamprath, editors, The role of phosphorus in agriculture. ASA, CSSA, and SSSA, Madison, WI. 263–310.

SAS Institute. 2011. The SAS system for Windows version 9.1.3. SAS Institute,Cary, NC.

Sharpley, A., and Tunney, H. 2000 Phosphorus research strategies to meet agricultural and environmental challenges of the 21st Century. J. Environ. Qual. 29: 176-181.

Soil Survey Laboratory Staff. 2004. Soil survey methods manual. Soil survey investigations Rep. No. 42 Version 4.0. National Soil Survey Center, Lincoln, NE.

Soil Survey Staff. 2011. Soil Survey Laboratory Information Manual. Soil Survey Investigations. Report No. 45, Version 2.0. R. Burt (ed.) U.S. Department of Agriculture, Natural Resources Conservation Service.

Sposito, G. 1989. The Chemistry of Soils. xiii 277 pp. New York, Oxford: Oxford University Press. ISBN 0 19 504615 3.

Stratful, I., M. D. Scrimshaw, and J. N. Lester. 2001. Conditions influencing the precipitation of magnesium ammonium phosphate. Water Res. 35: 4191–4199.

Szogi, A.A., M.B. Vanotti, and P.D. Shumaker. 2018. Economic recovery of calcium phosphates from swine lagoon sludge using Quick Wash process and geotextile filtration. Front. sustain. food syst. 2: 37.

Tran, A. T. K., Y. Zhang, D. De Corte, J. B. Hannes, W. Ye, P. Mondal, N. Jullok, B. Meesschaert, L. Pinoy, and B. Van der Bruggen. 2014. P-recovery as calcium phosphate from wastewater using an integrated selectrodialysis/crystallization process. J. Clean. Prod. 77: 140–151. https://doi.org/10.1016/j.jclepro.2014.01.069

USEPA. 2007. Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils and oils. Test methods. USEPA. http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3051a.pdf

Valsami-Jones, E., 2001. Mineralogical controls on phosphorus recovery from wastewaters. Mineral. Mag. 65: 611–620.

Velthof, G. L., M. L. van Beusichem, W.M.F. Raijmakers, and B. H. Janssen. 1998. Relationship between availability indices and plant uptake of nitrogen and phosphorus from organic products. Plant Soil. 200: 215–226.

Vogel, T., J. Kruse, N. Siebers, M. Nelles, and B. E. Löbermann. 2017. Recycled Products from Municipal Wastewater: Composition and Effects on Phosphorus Mobility in a Sandy Soil. J. Environ. Qual. 46: 443–451.

Wang, L., and G. H. Nancollas. 2008. Calcium Orthophosphates: Crystallization and Dissolution. Chem. Rev. 108(11): 4628–4669. https://doi.org/10.1021/cr0782574

Watson, M. E., and J. R. Brown. 1998. pH and lime requirement. In: J.R. Brown, editor, Recommended chemical soil test procedures for the north central region. Missouri Agric. Exp. Stn, Univ. of Missouri, Columbia, MO. 13–16.

Weeks, J., and G. M. Hettiarachchi. 2020. Source and Formulation Matter: New Insights into Phosphorus Fertilizer Fate and Transport in Mildly Calcareous Soils. Soil Sci. J. Am. 84: 731-746. https://doi.org/10.1002/saj2.20054

Werner, F. and J. Prietzel. 2015. Standard protocol and quality assessment of soil phosphorus speciation by P K-edge XANES spectroscopy. Environ. Sci. Technol. 49: 10521-10528.

Zarcinas, B.A., M.J. McLaughlin, and M.K. Smart. 1996. The effect of acid digestion technique on the performance of nebulization systems used in inductively coupled plasma spectrometry. Commun. Soil Sci. Plant Anal. 27:1331–1354.

Zhang, X., E. A. Davidson, T. Zou, L. Lassaletta, Z. Quan, T. Li, and W. Zhang. 2020. Quantifying Nutrient Budgets for Sustainable Nutrient Management. Global Biogeochem. Cycles. 34(3).

Zohar, I., M.S. Massey, J.A. Ippolito, and M.I. Litaor. 2018. Phosphorus sorption to aluminum-based water treatment residuals reacted with dairy wastewater: 1. Isotherms, XRD, and SEM-EDS analysis. J. Environ. Qual. 47: 538–545.

Chapter 5 - Exploring the potential of P based recovered nutrient products (RNPs) from swine wastewater in agriculture: Fate and behavior in a selected neutral soil

Abstract

Phosphorus (P) is crucial for crop growth and food security. Mined rock phosphate is the primary source of P fertilizer, but it will eventually become scarce. Recovered nutrient products (RNPs) from wastewater are a promising alternative as they contain high concentrations of plant-available nutrients such as P. This study evaluated the effectiveness of Ca-based RNPs, recovered from swine wastewater, using an innovative anaerobic membrane bioreactor (AnMBR) technology. The overall aims were to characterize the RNPs and compare the dissolution, transformations, and potential bioavailability of P in RNPs with conventional P fertilizers in a selected neutral soil using short-term laboratory incubation studies. The soil was incubated for 3-days, 1-week and 5-week in Petri dishes with four treatments: RNP, monoammonium phosphate (MAP), triple superphosphate (TSP), and control. After each incubation period, soil was sectioned at different distances from the point of application. Soil pH, total P (to assess the diffusion), and resin extractable P (to assess potential plant availability) were measured. Selected samples were also analyzed using X-ray absorption near edge structure (XANES) spectroscopy to identify the P speciation in tested soil. Phosphorus diffuses from the center section to the next section following the order of TSP>MAP>RNP. Resin extractable P (as % of total) was highest in the center section of MAP and TSP, followed by RNP and control after 5 weeks of incubation. Further, P reaction products showed differences in P speciation where the control soil was dominated by clay-Al adsorbed P species, the center sections of MAP

and TSP showed the majority of P in clay-Al adsorbed P or octa calcium phosphate (OCP) while the RNP showed more insoluble precipitated species like hydroxyapatite. Lack of solubility of RNP can be explained by alkaline effect of RNP on sol in the fertilized section. The results showed that Ca-based RNP acted as a slow-release P source for tested soil and showed lower solubility and extractability conventional fertilizers compared. Optimizing Ca-based RNP recovery may offer N free versatile secondary P sources to use in agriculture.

Introduction

Phosphorus (P) is a crucial macronutrient essential for all life forms. It is considered one of the most limiting nutrients in soil. It is also vital for optimal crop growth and development due to its role in numerous physiologic processes (Smil, 1999; Vance, 2001). On the other hand, P is used extensively in a variety of applications such as fertilizers, soft drinks, pharmaceuticals, biomaterials, and flame retardants (Qiu et al., 2019; Jupp et al., 2021; Duhamel et al., 2021). Low P availability in agricultural soil also reduces the efficient use of other essential plant nutrients. The decreased crop yields occurred due to reduced plant available P in soils over a growing season (Stoop, 1983). Despite the soil type, location, or the crop grown, a gradual decrease in P availability over time is an issue in agricultural soils. Therefore, to maintain adequate crop growth and yield, frequent or heavy P fertilizer applications may be necessary (Pierzynski, 1991). The primary source of P is the mining of phosphate rock. Such mineral phosphate rock reserves are predominantly located in just a handful of countries, increasing supply chain dependency and impacting global food security (Cordell & Neset, 2014; Blackwell et al., 2019). While mineral fertilizers are essential for optimum yields, plants utilize only some of the applied nutrients, and a large proportion is wasted or lost to the environment (Tilman et al., 2002). Environmental risks include eutrophication in surface waters from soil runoff erosion or subsoil leaching (Sharply et al., 2013; Andersson et al., 2015; Yan et al., 2016). Such fertilizer nutrient losses increase agricultural costs, waste energy, negatively impact global climate, and pollute the environment, thereby affecting the sustainability of modern agriculture (Chen et al., 2018).

The livestock sector, especially the swine industry, promotes agricultural development and a country's economy (Shin et al., 2005). However, due to an imbalance N: P ratio for crop

production, leading to excess P in soils and potential water pollution risks, land disposal of swine manure is an environmental concern (Szogi et al., 2018). Generally, other primary safety concerns associated with using animal manure as animal feed involve potentially harmful residues of pesticides, drugs, toxic minerals, and other toxins and the hazard of disease transmission (American Society of Animal Science, 1978; Hatfield et al., 1998).

The increasing demand for P sources and the sustainable management of nutrients in agricultural systems raises the need to effectively use soil P and P-containing mineral and organic fertilizers and move on to safe and efficient secondary P fertilizer sources. Therefore, recycling of P from municipal, agricultural, and other biodegradable waste sources as green renewable fertilizers with high P use efficiency has become highly important (Syers et al., 2008; Ma et al., 2011; Schroder et al., 2011; Huang et al., 2012; Zhang et al., 2013). Current wastewater treatment methods for P removal can be categorized as physical, biological, and chemical removal technologies. Physical technologies include adsorption, sand filtration for particulate P removal, ion exchange, and membrane filtration. Biological technologies include enhanced biological P removal, photosynthetic microbes immobilized on cellulose, ceramic or gel carriers, and phosphate-binding proteins (Azam et al., 2019; Kannan et al., 2023). The most common chemical technologies include precipitation by metal salts and lime addition, crystallization, coagulation, and flocculation (Azam et al., 2019; Kannan et al., 2023).

The Anaerobic Membrane Bioreactor (AnMBR) is a novel emerging technology that can facilitate the production of high-quality recovered nutrient products (Lim et al., 2019; Abuabdou et al., 2020). This wastewater treatment technology offers the benefit of controlled capture of N (as ammonium) and P (as orthophosphate) and simultaneous resource recovery as energy and water for indirect potable reuse (Kannan & Parameswaran, 2021; Liao et al., 2006; Lin et al.,

2013). This technology combines the techniques of anaerobic biological treatment and membrane filtration and uses different techniques such as coagulation, flocculation, chemical precipitation, and ion exchange to capture nutrients (Kannan & Parameswaran, 2021). Several studies by Lim et al., 2019 and Heronemus et al., 2021 have shown that chemical addition can be highly effective for P removal from AnMBR-treated municipal wastewater permeate. Several factors, including total alkalinity, pH, presence of impurities such as dissolved humic and fulvic acids, and interfering ions such as carbonate (CO_3^{2-}), aluminum (Al^{3+}), magnesium (Mg^{2+}) affect final fertilizer product quality (Cao & Harris, 2008; Zhou et al., 2015). Therefore, the composition of the treated wastewater significantly influences the type of final recovered nutrient products (RNP) formed and their subsequent reuse as fertilizers.

Most studies on phosphorus removal from animal wastewater, including swine and dairy wastewater, have focused on struvite recovery (Huang et al., 2016; Rabinovich et al., 2018; Le et al., 2021). Though struvite is the most common phosphate fertilizer product recovered from wastewater, several areas for improvement, such as high operational costs, high energy consumption, and large footprint of the recovery technologies (Ghosh et al., 2019). The addition of struvite causes the pH to increase naturally and has frequently been reported to perform as well as more conventional acidulated fertilizer products when ground and blended into soils (Sengupta & Pandit, 2011; Antonini et al., 2012; Ackerman et al., 2013; Degryse et al., 2017). However, when applied as granules, as dry fertilizers in agronomic situations, performance is often compromised (Ackerman et al., 2013; Talboys et al., 2016; Degryse et al., 2017; Everaert et al., 2017). There are limited studies on the exclusive recovery of calcium phosphate from swine wastewater (Szogi et al., 2018). Calcium phosphates recovered from wastewater have a P content comparable to mined rock phosphates, allowing their application as direct fertilizers or

raw materials for the fertilizer industry (Vasenko & Qu, 2017). Szogi et al., 2012 compared recovered Ca-P from swine and broiler manure to triple superphosphate (TSP) and fresh broiler litter in vertical column studies filled with sandy, coastal plains soil and found that when applied at a high rate (170 kgP_2O_5 ha^{-1}), all were able to supply cotton for the eight-week trial adequately; P uptake and biomass exhibited no significant difference. Plant availability of recycled P products derived from dairy effluents and pig manures was evaluated using pot and soil incubation experiments by Achat et al., 2014. The final quality of these recovered products is affected by the presence of suspended particles, heavy metals, and other impurities, and it is essential to remove the suspended particles before chemical addition to produce high-quality products (Ping et al., 2016).

A pilot-scale gas sparged AnMBR operated at Swine unit, Kansas State University and treated wastewater with seasonally varying temperatures that included dissolved methane recovery using a membrane contactor, sulfide and P recovery using coagulation, flocculation, and sedimentation and ammonia capture using a clinoptilolite IX column (Lim et al., 2019). When these P-rich RNPs are used as a soil amendment or fertilizer, understanding the potential availability of nutrients is essential. Characterizing these RNPs is critical as the nutrient contents in the RNPs may vary with the wastewater composition, characteristics, and the treatment technologies applied. Many techniques such as X-ray diffraction (XRD) (Ippolito et al., 2003; Massey et al., 2010; Zohar et al., 2018), scanning electron microscopy (SEM) examination coupled with energy dispersive X-ray spectroscopy (EDX) (Massey et al., 2010; Zohar et al., 2018; Battistoni et al., 2001), and X-ray absorption near-edge structure spectroscopy (XANES) (Massey et al., 2018; Massey, 2019) have been used in P recovery studies. Combining different techniques should enhance species identification with less uncertainty (Hettiarachchi et al., 2008;

Lombi et al., 2011; Milani et al., 2015). Evaluate the nutrient release, diffusion, and potential plant availability, soil incubation studies can be used (Lombi et al., 2004; Hettiarachchi et al., 2008; Pierzynski & Hettiarachchi, 2018; Weeks and Hettiarachchi, 2020; Heronemus et al., 2021). Limited data are available regarding the potential use of these RNPs in soils. Therefore, the overall aims of this study were to characterize and compare the Ca-based RNPs recovered from swine wastewater using an innovative anaerobic membrane bioreactor (AnMBR) technology. Dissolution, transformations, and potential bioavailability of P in RNPs were investigated with conventional P fertilizers in a selected neutral soil using short-term laboratory incubation studies combined with wet chemical and synchrotron-based x-ray techniques.

Materials and Methods

Recovered nutrient product recovery

The AnMBR-treated swine permeate was collected during the day of testing from a lab-scale AnMBR located at Kansas State University treating real swine lagoon wastewater. The lab scale AnMBR system had a COD removal efficiency of >80% and BOD removal efficiency of >95% under steady-state conditions. Several trails of coagulation experiments with real swine permeate collected from the lab scale AnMBR system were performed using 100% calcium oxide (CaO) and 50/50 calcium chloride/calcium oxide coagulant mixtures in varying molar ratios of Ca/P ranging from 1/1 to 12/1 as described in Kannan et al., 2023. Then, the permeate characteristics were altered to remove the carbonate alkalinity from the permeate solution. The pH was adjusted, and the permeate was aerated overnight to strip the CO_2 gas generated within the solution. Based on the results obtained by Kannan et al., 2023, RNPs were recovered at 100% CaO coagulant with 2/1 Ca/P ratio and used for further characterization and soil incubation studies.

Product characterization

A semi-solid nutrient-rich sample from real swine permeate was freeze-dried and digested in a microwave digestion unit using USEPA method SW846-3051A (USEPA, 2007). The major elemental composition was analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, 720-ES, Varian, Santa Clara, CA). The selected potentially toxic trace elemental composition was analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, 7500cx, Agilent, Santa Clara, CA). The pH of the freeze-dried product was measured in a 1:10 product: water extract. For the freeze-dried product, the 2% (w/v) citric acid solubility analysis was conducted using a modified method by the Association of Official Agricultural Chemists, 1945 to assess the agronomic value of RNPs as a fertilizer. A powder XRD analysis was done to identify existing nutrient phases in the RNPs using PANalytical Empyrean Multi-Purpose X-Ray Diffractometer (Spectris Company, Egham, Surrey, UK) using Cu Kα radiation at a wavelength of 1.54 Å and generator settings of 45 kV and 40 mA. Measurements were made using a continuous scanning technique from 5 to 70 °2θ and a scan speed of 0.024° per second. A Hitachi S-3500 N scanning electron microscope equipped with a Model S-6542 absorbed electron detector (Hitachi Science Systems, Ibaraki, Japan) at an accelerating potential of 5 kV was used for SEM-EDX spectroscopy analysis. The XANES spectroscopy at Sector 9-BM-B, Advanced Photon Source, Argonne National Laboratory, Argonne, IL was also used to characterize the product further. The RNP sample was diluted ten times using boron nitride to avoid self-absorption issues. A KBr Quick Press Kit (International Crystal Laboratories, Garfield, NJ) was used to make pellets of the RNP sample and carefully placed on a double-sided carbon tape (SPI Supplies, West Chester, PA), then on the sample holder and placed into a helium filled chamber for analysis. In fluorescence mode, six XANES

scans were collected for the sample at a range of 2.1 to 2.4 keV. All spectra, including the P_2O_5 standard used for energy calibration, were collected with a solid-state drift detector.

Edge energy was calibrated using phosphorus pentoxide (P_2O_5) and the background correction followed by the linear combination fitting of the reported spectra was done using in Athena (Ravel & Newville, 2005) according to the concepts of Werner & Prietzel, 2015. Previously collected P reference standards were also used, and the P_2O_5 standard spectra were collected during each run for any energy shifts.

Transformations, reaction pathways, and availability of RNP in soils

A neutral soil was sampled for the short-term laboratory incubation studies from the Agronomy North Farm, Manhattan, Kansas, USA (39°12'43.46"N 96°35'37.74"W). The soil was characterized as moderately well-drained Kennebec silt loam (fine-silty, mixed superactive, mesic Cumulic Hapludolls). Soil was collected at a 0-15 cm depth, air-dried, and sieved to <2mm. The maximum water-holding capacity was measured using the protocol from Jenkinson & Powlson, 1976. The pH of the soil was measured in a 1:10 soil: water extract (Watson & Brown, 1998). Displacement method was used to determine the cation exchange capacity (CEC) (Soil Survey Staff, 2011). The total P was determined using Zarcinas et al., 1996, which was modified to use a digestion block instead of a microwave. Available P was measured using Mehlich-3 P extraction as described in Frank et al., 1998. Total organic C and total N were determined via dry combustion method by Nelson & Sommers, 1996. Combination of a Method 3A-1 from the Soil Survey Laboratory's methods manual (Soil Survey Laboratory Staff, 2004) and a modification of the pipette method by Kilmer & Alexander, 1949 was used to determine the soil texture.

Petri dishes (87 mm diameter and 11 mm height) were packed to 1.1 g cm^{-3} desired bulk density with pre moist soil at 10% of the total deionized water needed to achieve 50% of maximum water-holding capacity. Desired water-content was achieved by adding remaining deionized water slowly onto the packed soil. Preliminary work showed that this bulk density was ideal for filling the volume of the petri dish without unnecessary compression. Parafilm (Bemis Flexible Packaging, Neenah, WI) were used to wrap the plates and they left to equilibrate at room temperature for 24 h. The plates were unwrapped. Then the powdered treatments were placed just below the soil surface, in the center of the plate, and covered with soil. As the RNP was recovered in powder form all other treatments were also added in the same way. The four treatments with four replicates as follows:

i. Unfertilized control soil sample;

ii. Monoammonium phosphate (MAP, 11:23:0; 11% N–23% P–0% K2O by weight): 7.5 mg P;

iii. Triple superphosphate (TSP, 0:20:0; 0% N–20% P–0% K2O by weight): 7.5 mg P; and

iv. RNP (11.1% P by weight): 7.5 mg of P.

Petri dishes were closed, wrapped individually with Parafilm and stacked. Then stacked dishes were wrapped again in aluminum foil. They incubated (Precision Low Temp Incubator, Waltham, MA) in the dark at 25 °C. Incubation study was conducted for three incubation periods of 3-days, 1-week, and 5-weeks and consisted of 3 separate sets for each period. Plates were opened at the end of each period and soil was collected from 0 to 7.5, 7.5 to 13.5, 13.5 to 25, and 25 to 43.5mm, from the point of application as concentric rings starting from the center. Each sample was placed in a pre-weighed plastic specimen container (Fisher Scientific, Waltham, MA). The weighed samples were oven-dried at 40 °C (Fisher Scientific drying oven, Waltham, MA). After drying, weight was recorded, and soil was ground gently with a mortar and pestle.

Aqua regia digestion (without H_2O_2 pretreatment) was used to determine the total P for all samples and analyzed via ICP-OES. Total P data were normalized by calculating the percentage of P added (PPA) for each dish section for all treatments is defined as follows (Hettiarachchi et al., 2010):

$$PPA = \frac{(P_f)S_i \times M_i}{\sum_{i=1-4}[(P_f)S_i \times M_i]} \times 100$$

where *i* is the dish section (1–4), (P_f)*S*i is the concentration of P fertilizer in each dish section, and *M*i is the mass of soil in each dish section. (P_f)*S*i is calculated by subtracting the total P concentration of the unfertilized soil sample from the total P concentration in the fertilized dish section.

The Anion exchange resin (AER) technique (Myers et al., 2005) was used to determine the resin extractable P (potentially plant available) and quantified colorimetrically using a Beckman-Coulter DU-800 spectrophotometer (Brea, CA) (Murphy & Riley, 1962). Percentage of resin P (PRP) for each dish section for all treatments were calculated according to the following equation (Pierzynski & Hettiarachchi, 2018):

$$PRP = \frac{REP_i}{Total\ P_i} \times 100$$

where *i* is the dish section (1–4), REP_i is the resin P concentration, and $Total\ P_i$ is the total P concentration in the i^{th} dish section.

X-ray absorption near-edge structure analysis was performed for the composite samples of the 0- to 7.5 mm, and 7.5-13.5 mm sections, prepared using equal masses of soil from the four replicates used for chemical analysis. The P K-edge XANES data were collected at Sector 9-BM-B, Advanced Photon Source, Argonne National Laboratory, Argonne, IL. All spectra,

including the P_2O_5 standard used for daily monochromator alignment, were collected with a solid-state drift detector in fluorescence mode. The soils were ground to <150 mm in an agate mortar and pestle, then a 7-mm soil pellet was prepared from the soil with the KBr Quick Press Kit (International Crystal Laboratories, Garfield, NJ) and carefully mounted on the sample holder with double-sided carbon tape (SPI Supplies, West Chester, PA). Six scans were collected for each P treated sample, and 12 were collected for each control sample.

Background correction and linear combination fitting of the experimental spectra were completed in Athena (v.0.9.25) (Ravel & Newville, 2005) according to the concepts set forth by Werner & Prietzel, 2015. Previously collected P reference standards were also used, and the P_2O_5 standard spectra were collected during each run for spectral alignment. Briefly, six or twelve scans were merged to limit noise. Pre-edge and normalization ranges were not fixed, allowing for each sample's maximized fit. All spectra were adjusted such that E_0 of 2149 eV corresponded to one-half the height of the white line peak. Reference spectra were eliminated if they comprised <5% of the calculated composition and the fitting was repeated.

Statistical analysis

All soil wet chemical data were analyzed in SAS (SAS Institute, 2011) through the Proc MIXED procedure. The experimental design was a complete randomized design. Data were analyzed via ANOVA with P fertilizer treatment as the main treatment, and dish sections as subplot treatments. The Tukey's HSD test was used to compare all treatments at an $p = 0\ .05$ level of significance.

Results and Discussion

Characterization of the recovered nutrient product

The RNP was rich in Ca and P, comprising approximately 22% and 11%, respectively (Table 5.1). Product pH (1:10 product: water) was 8.3, alkaline. Significant amounts of Ca in this RNP were predominantly from adding calcium oxide coagulant. Several authors noted that higher pH levels could cause readily precipitation of calcium phosphate products (Lei et al., 2017; Tran et al., 2014; Wang & Nancollas, 2008). The total P content in this RNP (11%) is comparable to other wastewater-derived nutrient products reported in previous studies. Cunha et al., 2020 reported that a study treating black water recovered CaP granules with 10 ± 2 % of average total P. Szogi et al., 2018 reported swine lagoon sludge-derived products with a total P content of 14.5 % - 15.5 %. Rech et al., 2018 recovered struvite from swine wastewater containing 12.8 % of total P. Sewage wastes and animal manures generally have lower total and water-soluble P concentrations than mineral P fertilizers and contain varying amounts of organic P and other elements that may affect P availability to plants (Hedley & McLaughlin, 2005). Cunha et al., 2020 reported that the potential presence of heavy metals, organic micropollutants, and pathogens recovered products from waste streams raises concerns. The measured trace element concentrations of the RNP were low (Table 5.1).

Table 5.1. Selected major and trace elemental composition of the recovered nutrient product.

Major Element†	% (w/w)	Trace Element‡	mg kg^{-1}
P	11.1±0.02	**Zn**	14.4±0.02
Ca	22.4±0.01	**Cr**	9.6±0.01
Mg	1.0±0.00	**Se**	3.4±0.01
S	0.8±0.01	**As**	1.6±0.01
K	0.3±0.01	**Pb**	0.8±0.00
Fe	0.1±0.00	**Cd**	0.01±0.00
Al	0.1±0.00	**Mo**	<DL*

†Measured using inductively coupled plasma optical emission spectrometer (ICP-OES)
‡Measured using inductively coupled plasma mass spectrometer (ICP-MS)
* Below the detection limit of ICP-MS, 0.01 mg kg^{-1}

This RNP's 2% (w/v) citric acid solubility (as a % of total P) was 11%. As a reference, soft rock phosphate and TSP have about 30% and 88% of citric acid solubility of total P, respectively (Christiansen et al., 2020). Factors, such as crystallinity of the product and the substitution of ions such as Al and Fe, affect the citric acid solubility of P sources (Braithwaite & Eaton, 1990).

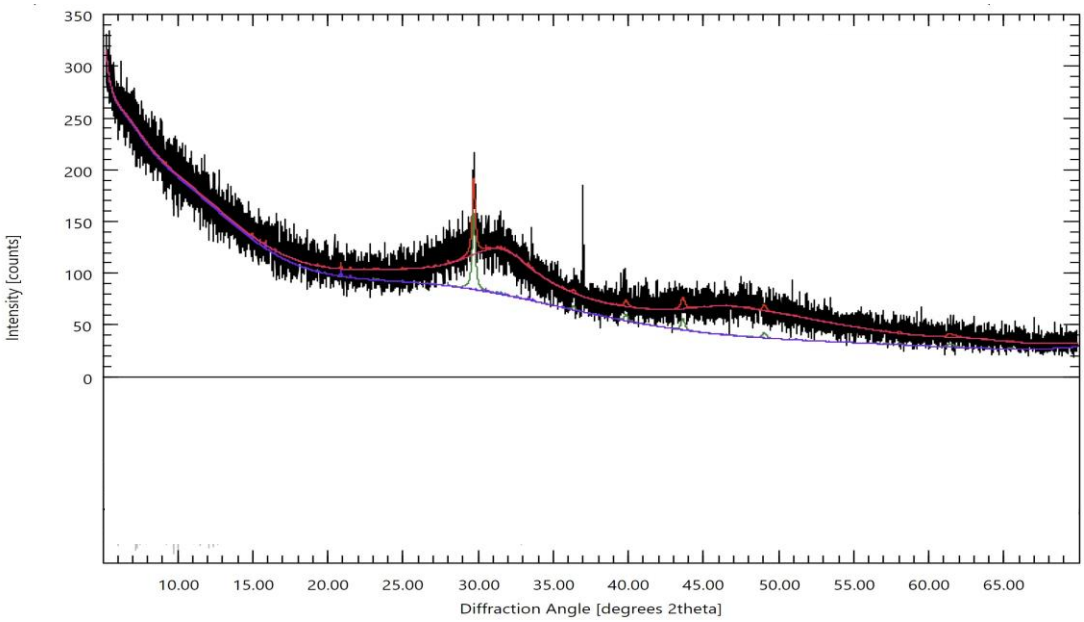


Figure 5.1. The X-ray diffractogram of the recovered nutrient product

The XRD technique provides insights into crystalline structures, and its detection limit is about 2 wt.% of the sample (Klug & Alexander. 1974; Ali et al., 2022). The XRD pattern had a broad peak between 25° and 35° 2θ position (Figure 5.1) and was at a similar peak position as the prominent hydroxyapatite peak (Liu & Lal, 2014). Dorozhkin, 2010 and Daneshgar et al., 2018 also reported similar amorphous P phases within those peak positions. Therefore, the enhanced background and broader peak suggested the potential presence of hydroxyapatite and the product's amorphous nature. The conditions of formation of the recovered products result in physical and chemical differences in the products (Massey et al., 2010). Factors like retention time and complexity of the wastewater matrices could interfere with the crystallization process (Stratful et al., 2001; Valsami-Jones, 2001; Le Corre et al., 2005).

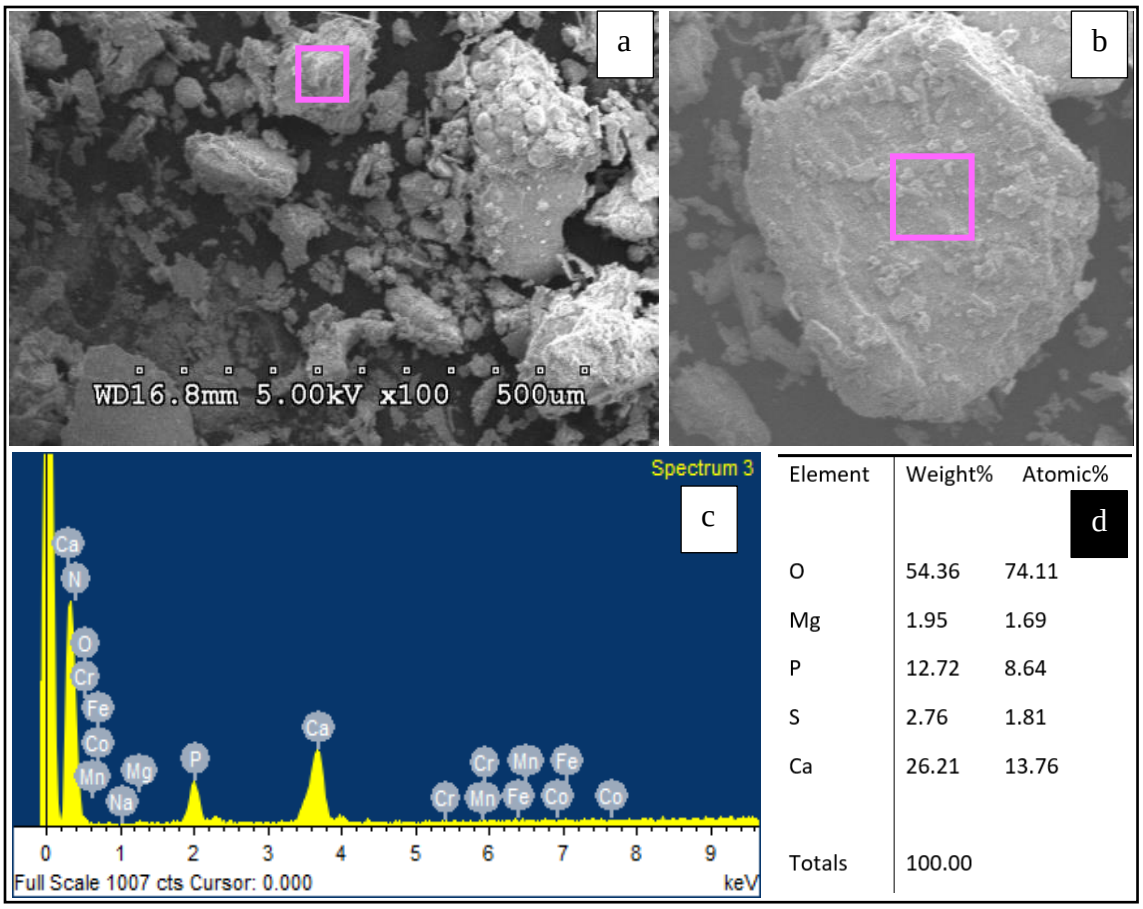


Figure 5.2. (a) Backscattered electron (BSE) image of the recovered nutrient product (RNP). The area selected to zoom in more, is outlined in pink. (b) The BSE images of the zoomed in RNP particle. The area selected to do the elemental analysis is outlined in pink. (c) Elemental composition of the selected area by energy dispersive X-ray spectroscopy. (d) Table of elemental composition of the (c).

The SEM image in Figure 5.2a showed that the particles had an irregular shape and homogeneous nature. The data collected from a selected particle from backscattered electron (BSE) images-energy dispersive X-ray (EDX) (Figure 5.2b) showed that the product is rich in Ca and P (Figure 5.2c and 5.2d). The main application of SEM-EDX was traditionally in the field of morphological characterization and qualitative elemental analysis (Speiser et al., 2001). The atomic number sensitivity of BSE images can differentiate particles with different chemical compositions, and the EDX allows us to get the elemental composition on the surface. Regions

of high average atomic number will appear bright relative to regions of low atomic number. The results confirmed the presence of high Ca in the product. Bowers et al., 2007 reported the struvite's SEM-EDX images, which showed that Mg phosphate crystals precipitated on the Ca phosphate seed material surface. Studies of P recovery processes tend to perform some product characterization, including SEM-EDX (Massey et al., 2010; Battistoni et al., 2001, 2005; Wu & Bishop, 2004; Wang et al., 2005; Le Corre et al., 2007).

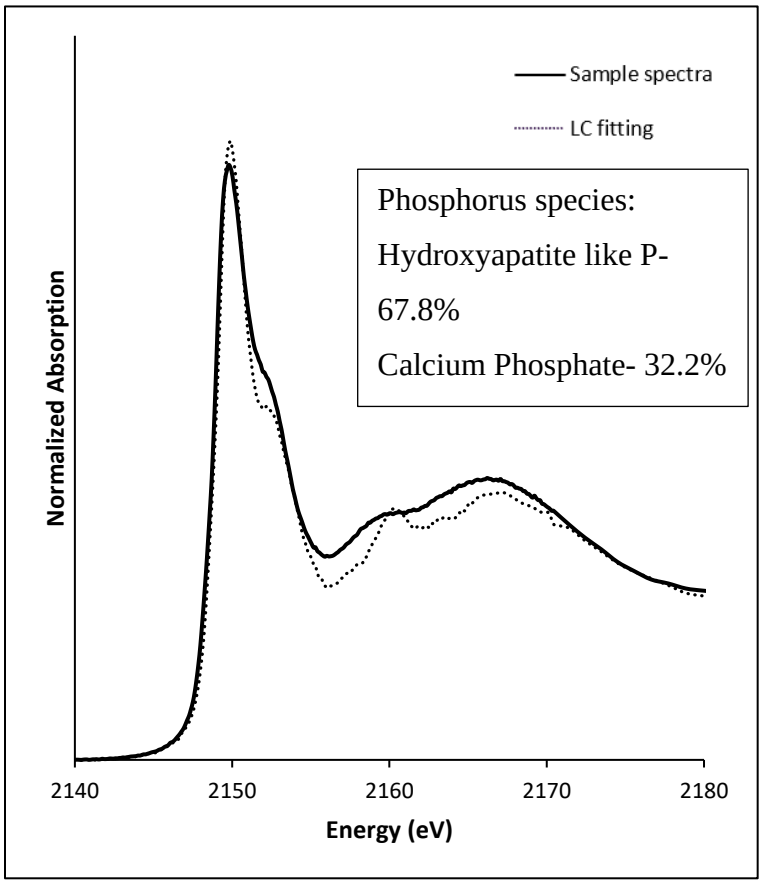


Figure 5.3. Normalized P K-edge X-ray absorption near edge structure spectra with results of linear combination fitting for the recovered nutrient product.

The X-ray absorption near-edge structure spectroscopy analysis of the RNP (Figure 5.3) also showed that hydroxyapatite-like P solid dominated the P speciation (~68%). The residual (minor un-fitted parts) might result from the product's heterogeneous nature and not having a

well-defined crystalline structure. The XANES results confirmed the composition of this RNP. Massey, 2019 used P K-edge XANES spectra and reported that the recovered dittmarite appeared pure, and the crystalline struvite materials recovered from dairy wastewater had 17% apatite and 83% struvite. Heronemus et al., 2021 also used the bulk P K-edge XANES spectra on RNP recovered from municipal wastewater and showed that the product is rich in iron adsorbed-P, especially goethite sorbed-P and vivianite-like P.

The amorphous nature of this product suggests that it could have better P dissolution and greater plant P bioavailability and uptake. However, recovered P availability and P uptake by crops depend significantly on soil conditions, the type of P fertilizer applied, and specific crop characteristics (Massey et al., 2009; Antonini et al., 2012; Vogel et al., 2017). Le Corre et al., 2007 identified the size, purity, and morphology of recovered materials as critical factors in the materials' successful recovery and reuse as fertilizer. These RNPs could be a good candidate for direct fertilizer application depending on soil and crop types.

Distribution, transformations and potential bioavailability of P in RNPs in soil

Short-term laboratory incubation studies were conducted to understand the distribution, transformations, and potential bioavailability of P in RNPs in soil. Selected physical and chemical properties of the soil used for the incubation studies (Table 5.2) showed that the initial soil pH was neutral, and the soil had a sandy loam texture.

Table 5.2. Selected physical and chemical properties of the soil used for the incubation study.

Parameter	Value
pH (1:10 soil:water)	7.2±0.1
CEC, $cmol_c$/kg	16.3
Total P, mg/kg	429±2
Mehlich III P, mg/kg	79.0
Resin extractable P, mg/kg	27.7±0.3
Total C, %	3.32
Total N, %	0.28
Texture	Silt loam
(Sand, silt, clay %)	(9, 69, 22)

Diffusion of P

In this tested neutral soil, after 3 days of incubation, all treatments were diffused to the second section, where more than 95% of RNP was still retained in the center section (Figure 5.4). The P diffusion increased over time, and at the end of 5 weeks, MAP and TSP diffused till the third section, where RNP diffusion was only from the center to the second section (Figure 5.4). The enhanced diffusion of MAP and TSP could be attributed to the initial acidulation effect of those treatments (Figure 5.5). In neutral-to-calcareous soils, P retention is dominated by precipitation reactions (Lindsay et al., 1979), although P can also be adsorbed on the surface of

Ca. The P diffusion from fertilizer is usually assessed by sampling the soil in sections around the fertilizer application site after a given incubation time (Degryse & McLaughlin., 2014). Lombi et al., 2004, 2005 compared granular and fluid fertilizers in a range of soils by measuring total and isotopically exchangeable in four concentric sections around the fertilizer application site at 35 d after application. McBeath et al., 2012 used this method to assess the diffusion of P and Zn from fertilizer under wet or dry conditions. These studies have shown that diffusion of P from a fertilizer granule is often mostly restricted to within a few centimeters of the granule several weeks after application, except in soil with low P retention (Lawton & Vomocil, 1954; Lombi et al., 2005). In neutral soil, three waste-derived struvite showed much less P diffusion than MAP in a petri dish diffusion experiment conducted by Degryse et al., 2017. In the center section of the RNP-added treatment, a higher amount of Ca could increase P reactions with Ca per soil volume and decrease average solution P concentrations. The decreased solution concentration would reduce the gradient slope and potentially slow overall diffusion (Weeks & Hettiarachchi, 2020; Olsen & Watanabe, 1963).

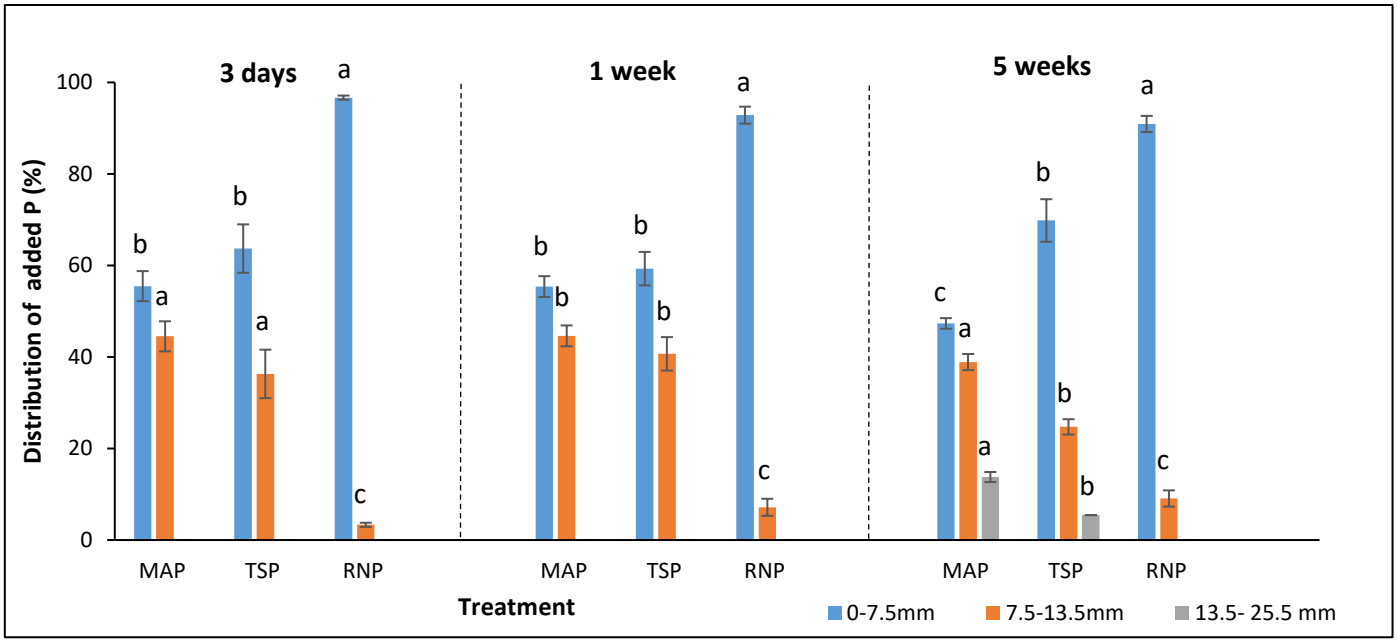


Figure 5.4. Distribution of added P (%) after 3 days, 1 week, and 5 weeks of incubation in neutral soil. Means within a soil section for each treatment each time period containing the same letter are not significantly different at $p = 0.05$ according to Tukey's pairwise method.

Potential plant available P and pH

The center section of MAP and TSP added treatments showed higher PRP than the center section of RNP and control after 3 days of incubation (Figure 5.5). However, after 1 week of incubation, PRP in the center section of RNP was higher than the control (Figure 5.5). The trend continued for 5 weeks, and the highest PRP in the center section was by MAP and TSP, followed by RNP and control. Also, after 5 weeks, MAP and TSP showed increased PRP in the second and third sections compared to control (Figure 5.5). Although ~ 14- 45% of P diffused into the second section by 1 week, the PRP in the second section for all the treatments was not significantly different from the control (Figure 5.5), suggesting strong P sorption. Phosphorus is adsorbed onto calcium carbonate in alkaline soils and surfaces of clay and amorphous Al or Fe oxides in acid soils. According to Sposito, 1989, most adsorbed P in soil occurs as inner-sphere complex species (specific adsorption), and some P is adsorbed as either diffuse ion swarm or

outer-sphere complex species (nonspecific adsorption). Inner-sphere complex P is slower to equilibrate with the soil solution P than the outer sphere and diffuse swarm P (Khatiwada et al., 2012). Therefore, even if the P is moved, they might not be available.

The maximum pH reduction was observed in the center section of MAP and TSP and, as moving away from the center, pH became similar to the control soil pH in all time durations (Figure 5.5). The fertilizer MAP contains ammonium N. Nitrification of ammonium-N contained within the P fertilizers results in acidification (Hanson & Westfall, 1985). The indirect nature of soil acidification by MAP causes it to persist longer than TSP. According to Lindsay, 1979, the dissolution of TSP causes direct soil acidification, which results in higher solubility and, therefore, greater P availability. Recovered nutrient products buffered the soil pH in the center section around 7.8, closer to the RNP's original pH even after 5 weeks of incubation. The presence of excess Ca salts (i.e., excess base) added during the production process could lead to suppression of dissolution of RNP, whose speciation is also dominated by Ca-P. Degryse et al., 2017 also showed that excess base in the waste recovered struvite reduced its dissolution rate in soil, and it depends on the soil properties such as pH buffering capacity. However, PRP from the RNP in the center section was higher than the control.

In this control soil, Mehlich III P was in the higher range. Therefore, there is no need for a P source that will be available immediately or P at all. In that case, this Ca-based RNP, which showed lower solubility and extractability, would be a better option when selecting a better P source for this soil.

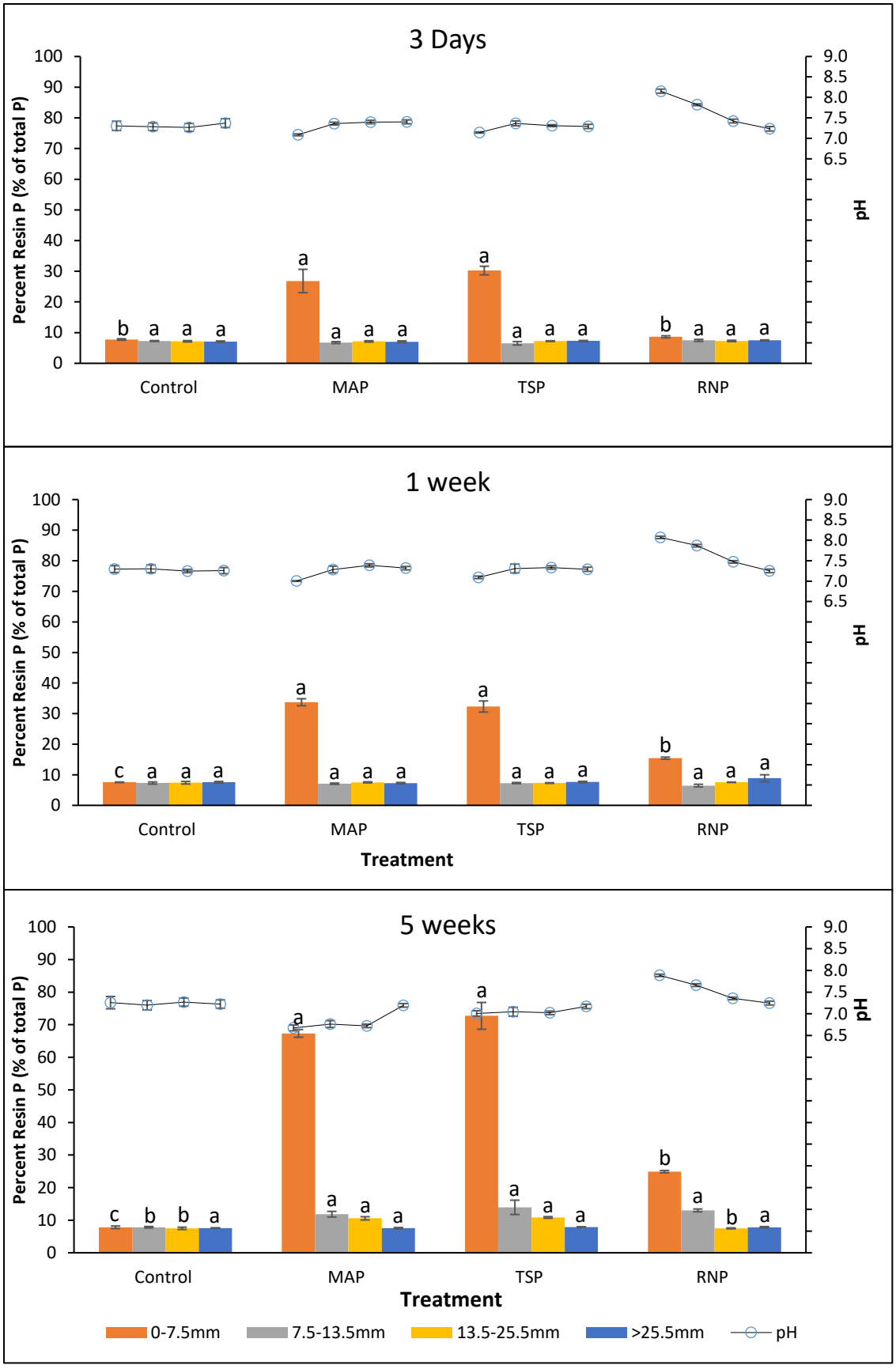

3 Days
1 week
5 weeks
Percent Resin P (% of total P)
pH
Control
MAP
TSP
RNP
Treatment
0-7.5mm
7.5-13.5mm
13.5-25.5mm
>25.5mm
pH

Figure 5.5. Percent resin P (PRP) and the pH for each dish section for all treatments after 3 days, 1 week and 5 weeks of incubation in neutral soil. Means within a soil section for each treatment containing the same letter are not significantly different at $p = 0.05$ according to Tukey's pairwise method.

Reaction products of P

The XANES technique helps determine an element's local chemical and structural environment and oxidation state (Fendorf & Sparks, 1996). It facilitates the identification of the speciation. It is used to identify contaminants and nutrients in soils, which determines their availability and fate in the environment. This technique is widely used for speciating organic and inorganic P in soils, sediments, agricultural byproducts, and fertilized soils (Hesterberg et al., 1999; Peak et al., 2002; Beauchemin et al., 2003; Khatiwada et al., 2012; Lombi et al., 2006; Kruse & Leinweber, 2008; Weeks & Hettiarachchi, 2020).

In the neutral soil, the control was dominated by clay-Al adsorbed P species (Figure 5.6). The center sections of MAP and TSP also showed the majority of P in clay-Al adsorbed P or octa calcium phosphate (OCP). As expected from the low resin extractable P results and lack of P diffusion, the RNP added treatment center section was dominated by more insoluble precipitated species like hydroxyapatite, explaining the reason for reduced solubility. The presence of adsorbed P species in both MAP and TSP treatments may be the reason for the increased PRP in the center dish section compared to RNP. Khatiwada et al., 2012 conducted a field study with reduced tillage to study P availability at various distances from either deep-banded or broadcast MAP P fertilizers and technical grade MAP added in liquid form and the reaction products formed within a Mollisol. Results showed that the resin-extractable P and speciation results were positively correlated, which indicates that the adsorbed P species could be more available. In RNP, alkaline pH restricts solubility (mobility) and resin extractability. Speciation of P in neutral

soil treated with RNP indicated that its speciation did not change much in the soils, likely due to its original speciation combined with residual alkalinity.

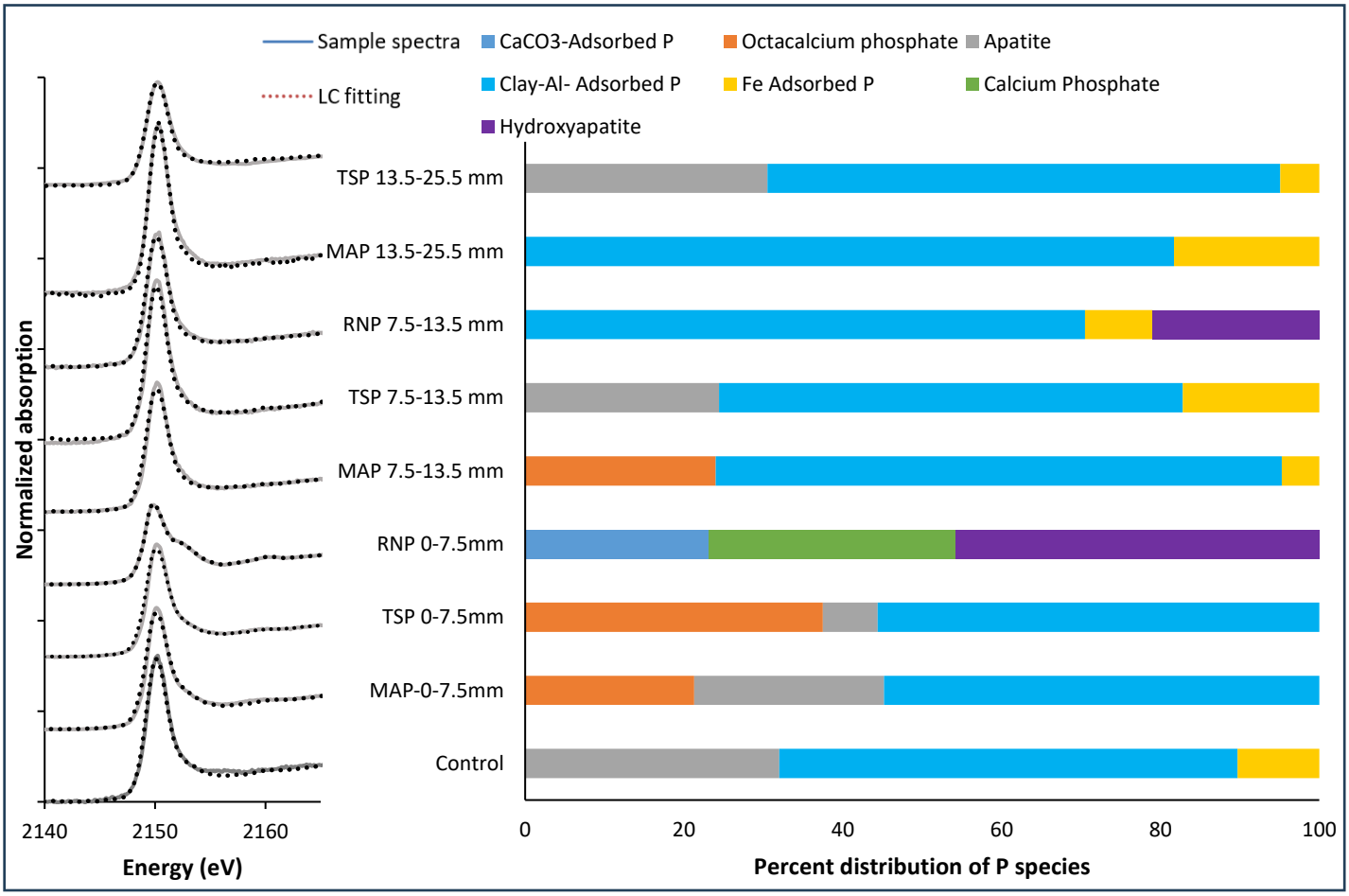


Figure 5.6. Normalized P K-edge X-ray absorption near edge structure spectra of selected dish sections with results of linear combination fitting as a percent distribution of P species in neutral soil.

Usability of the recovered Ca-P products

As mentioned earlier, recovery of P from animal wastewater is mainly focused on struvite recovery (Huang et al., 2016; Rabinovich et al., 2018; Le et al., 2021) with their production and potential reuse in agriculture (Bowers & Westerman, 2005; Suzuki et al., 2005). There is minimal focus on calcium phosphate recovery and reuse (Johnston & Richards, 2003;

Romer, 2006). Compared to struvite, in Ca- P products, N and P can be separated ($NH4^+$, which undergoes nitrification), which is a good thing as N will be easily lost if applied at planting or in the fall. Cunha et al., 2020 also reported that recovery of P as calcium phosphates enables the formulation of fertilizers with a more specific N:P ratio, in contrast to struvite (Cunha et al., 2020), which is beneficial. Also, it allows the blending of CaP granules with phosphate rock in the fertilizer industry to produce water-soluble phosphate (Schipper et al., 2001). Though the solubility of amorphous calcium phosphate materials has yet to be well studied, Valsami-Jones, 2001 reported that amorphous calcium phosphates were generally more soluble than crystalline forms. Bauer et al., 2007 documented that the recovered calcium phosphate was an effective fertilizer in a greenhouse study. The current study showed the low solubility and the slow release of P from recovered calcium phosphates, which could benefit specific crops and soils. Their use should also be encouraged in farming lands vulnerable to fertilizer runoff and surface water eutrophication mainly due to increased dissolved reactive P (Omo-Okoro et al., 2023). The low solubility property may offer an edge over conventional P fertilizers regarding building soil P levels and enabling plant growth.

Additionally, Cunha et al., 2018a also reported that the P removal capacity is similar for CaP granulation and struvite precipitation. Also, CaP granulation showed a more cost-effective and efficient alternative for P recovery in source-separated sanitation (Roefs et al., 2017; Cunha et al., 2020). Therefore, calcium phosphates show promising ability to be used as an alternative P source.

Summary

As society continues to focus on recovering P from waste streams and reusing it in agricultural production, assessing the P content of potential fertilizers and gaining a deeper understanding of the P speciation and their behavior in different soils is essential. The findings of this study showed that RNP recovered from swine wastewater acted as a P source for the tested neutral soil. The P diffusion and percent resin extractable P results showed that the RNP solubility was lower than the tested conventional fertilizers (MAP and TSP). The P speciation in both RNP and RNP added soils showed that the speciation was dominated by the hydroxyapatite like species which explains the reduced solubility and extractability of RNP in the tested neutral soil. Soil pH changes suggested that low solubility is partly due to residual alkalinity of the RNP. Low solubility and the slow release of P in RNP are helpful in different agricultural production systems. Optimizing Ca-based RNP recovery may offer useful and versatile secondary P sources that are not N-based, such as struvite to use in production agriculture.

References

Abuabdou, S. M. A., W. Ahmad, N. C. Aun, M. J. Bashir. 2020. A review of anaerobic membrane bioreactors (AnMBR) for the treatment of highly contaminated landfill leachate and biogas production: Effectiveness, limitations and future perspectives. J. Clean. Prod. 255: 120215.

Achat, D. L., M. Sperandio, M. L. Daumer, A. C. Santellani, L. Prud'Homme, M. Akhtar, and C. Morel. 2014. Plant-availability of phosphorus recycled from pig manures and dairy effluents as assessed by isotopic labeling techniques. Geoderma. 232–234: 24–33.

Ackerman, J. N., F. Zvomuya, N. Cicek, and D. Flaten. 2013. Evaluation of manure-derived struvite as a phosphorus source for canola. Can. J. Plant Sci. 93: 419-424.

Ali, A., Y.W. Chiang, and R.M. Santos. 2022. X-ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions. Minerals. 12: 205. https://doi.org/10.3390/min12020205

American Society of Animal Science. 1978. Response to FDA statement, "recycling animal waste." American Society of Animal Science, Champaign, IL.

Andersson, H., L. Bergström, B. Ulén, F. Djodjic, and H. Kirchmann. 2015. The role of subsoil as a source or sink for phosphorus leaching. J. Environ. Qual. 44: 535-544.

Antonini, S., M.A. Arias, T. Eichert, and J. Clemens. 2012. Greenhouse evaluation and environmental impact of different urine-derived struvite fertilizers as phosphorus sources for plants. Chemosphere. 89: 1202-1210.

Association of Official Analytical Chemists, H.A. Lepper. 1945. Official methods of analysis.

Azam, H.M., S.T. Alam, M. Hasan, D.D.S. Yameogo, A.D. Kannan, A. Rahman, and M. J. Kwon. 2019. Phosphorous in the environment: characteristics with distribution and effects, removal mechanisms, treatment technologies, and factors affecting recovery as minerals in natural and engineered systems. Environ. Sci. Pollut. Res. 26(20): 20183–20207.

Battistoni, P., A. De Angelis, P. Pavan, M. Prisciandaro, and F. Cecchi. 2001. Phosphorus removal from a real anaerobic supernatant by struvite crystallization. Water Res. 35: 2167–2178.

Battistoni, P., R. Boccadoro, F. Fatone, and P. Pavan. 2005. Auto-nucleation and crystal growth of struvite in a demonstrative fluidized bed reactor (FBR). Environ. Technol. 26: 975–982.

Bauer, P.J., Szogi, A.A., Vanotti, M.B., 2007. Agronomic effectiveness of calcium phosphate recovered from liquid swine manure. Agron. J. 99: 1352–1356.

Beauchemin, S., D. Hesterberg, J. Chou, M. Beauchemin, R.R. Simard and D.E. Sayers. 2003. Speciation of phosphorus in phosphorus-enriched agricultural soils using X-ray absorption near-edge structure spectroscopy and chemical fractionation. J. Environ. Qual. 32: 1809-1819.

Blackwell, M., T. Darch, and R. Haslam. 2019. Phosphorus use efficiency and fertilizers: future opportunities for improvements. Front Agric Sci Eng. 6(4): 332–340.

Bowers, K.E., and P.W. Westerman. 2005. Performance of cone-shaped fluidized bed struvite crystallizers in removing phosphorus from wastewater. Trans. ASAE 48: 1227–1234.

Bowers, K.E., T. Zhang, and J.H. Harrison. 2007. Phosphorus removal by struvite crystallization in various livestock wastewaters. In: Proceedings of International Symposium on Air Quality and Waste Management for Agriculture. American Society of Agricultural and Biological Engineers Meeting Paper No. 701P0907cd. St. Joseph, Mich., ASABE.

Braithwaite, A., and P. Eaton. 1990. Groom Factors affecting the solubility of phosphate rock residues in 2% citric acid and 2% formic acid. Fertilizer research. 23(1): 37-42.

Cao, X., and W. Harris. 2008. Carbonate and Magnesium Interactive Effect on Calcium Phosphate Precipitation. Environ. Sci. Technol. 42(2): 436–442.

Chen, J., S. Lü, Z. Zhang, X. Zhao, X. Li, P. Ning, and M. Liu. 2018. Environmentally friendly fertilizers: A review of materials used and their effects on the environment. Sci. Total Environ. 613-614: 829–839.

Christiansen, N. H., P. Sørensen, R. Labouriau, B.T. Christensen, and G.H. Rubæk. 2020. Characterizing phosphorus availability in waste products by chemical extractions and plant uptake. J. Plant. Nutr. Soil Sci. 183(4): 416-428.

Cordell, D., and T.S. Neset. 2014. Phosphorus vulnerability: a qualitative framework for assessing the vulnerability of national and regional food systems to the multidimensional stressors of phosphorus scarcity. Glob. Environ. Change. 24: 108–122.

Cunha, J. R., C. Schott, R.D. van der Weijden, L.H. Leal, G. Zeeman, and C. Buisman. 2020. Calcium phosphate granules recovered from black water treatment: A sustainable substitute for mined phosphorus in soil fertilization. Resour Conserv Recycl. 158: 104791.

Cunha, J.R., Schott, C., van der Weijden, R.D., Leal, L.H., Zeeman, G., Buisman, C. 2018a. Calcium addition to increase the production of phosphate granules in anaerobic treatment of black water. Water Res. 130: 333–342.

Daneshgar, S., A. Buttafava, D. Capsoni, A. Callegari, and A. Capodaglio. 2018. Impact of pH and Ionic Molar Ratios on Phosphorous Forms Precipitation and Recovery from Different Wastewater Sludges. Resources. 7(4): 71.

Degryse, F., and M.J. McLaughlin. 2014. Phosphorus Diffusion from Fertilizer: Visualization, Chemical Measurements, and Modeling. Soil Sci. Soc. Am. J. 78, 832–842.

Degryse, F., R. Baird, R.C. da Silva, and M.J. McLaughlin. 2017. Dissolution rate and agronomic effectiveness of struvite fertilizers – effect of soil pH, granulation and base excess. Plant Soil. 410: 139-152.

Dorozhkin, S.V. 2010. Amorphous calcium (ortho)phosphates. Acta Biomater. 6(12): 4457–4475.

Duhamel, S., J.M. Diaz, J.C. Adams, K. Djaoudi, V. Steck, and E.M. Waggoner. 2021. Phosphorus as an integral component of global marine biogeochemistry. Nat. Geosci. 14(6): 359–368.

Everaert, M., F. Degryse, M.J. McLaughlin, D. De Vos, and E. Smolders. 2017. Agronomic effectiveness of granulated and powdered P-exchanged Mg-Al LDH relative to struvite and MAP. J. Agric. Food Chem. 65: 6736-6744.

Fendorf, S.E., and D.L. Sparks. 1996. X-ray absorption fine structure. 378-416. In D.L. Sparks (ed.) Methods of soil analysis. Part. 3. SSSA, Madison, WI.

Frank, K., D. Beegle, and J. Denning. 1998. Phosphorus. In: J.R. Brown, editor, Recommended chemical soil test procedures for the north central region. Missouri Agric. Exp. Stn. University of Missouri, Columbia, MO. 21–30.

Ghosh, S., S. Lobanov, V.K. Lo. 2019. An overview of technologies to recover phosphorus as struvite from wastewater: advantages and shortcomings. Environ. Sci. Pollut. Res. 26(19): 19063–19077.

Hanson, R.L., and D.G. Westfall. 1985. Orthophosphate solubility transformations and availability from dual applied nitrogen and phosphorus. Soil Sci. Soc. Am. J. 49: 1283–1289.

Hatfield, J.L., M.C. Brumm, and S.W. Melvin. 1998. Swine Manure Management: Agricultural Uses of Municipal, Animal, and Industrial Byproducts. USDA Agricultural Research Service. Conservation Research Report No. 44.

Hedley, M., and M. McLaughlin. 2005. Reactions of Phosphate Fertilizers and By-Products in Soils, in Sims, T. J., Sharpley, A. N. (eds.): Phosphorus: Agriculture and the Environment. ASA, CSSA, SSSA, Madison, WI, USA. 181–251.

Heronemus, E., K. H.H. Gamage, G. M. Hettiarachchi, and P. Parameswaran. 2021. Efficient recovery of phosphorus and sulfur from Anaerobic Membrane Bioreactor (AnMBR) permeate using chemical addition of iron and evaluation of its nutrient availability for plant uptake. Sci. Total Environ. 783: 146850, https://doi.org/10.1016/j.scitotenv.2021.146850.

Hesterberg, D., W.Q. Zhou, K.J. Hutchison, S. Beauchemin, and D.E. Sayers. 1999. XAFS study of adsorbed and mineral forms of phosphate. J. Synchrotron Radiat. 6: 636-638.

Hettiarachchi, G.M., E. Lombi, M. McLaughlin, D. Chittleborough, and C. Johnston. 2010. Chemical behavior of fluid and granular Mn and Zn fertilisers in alkaline soils. Soil Res. 48: 238–247.

Hettiarachchi, G.M., M.J. McLaughlin, K.G. Scheckel, D.J. Chittleborough, M. Newville, S. Sutton, E. Lombi. 2008. Evidence for different reaction pathways for liquid and granular micronutrients in a calcareous soil. Soil Sci. Soc. Am. J. 72: 98–110.

Huang, H., P. Zhang, Z. Zhang, J. Liu, J. Xiao, and F. Gao. 2016. Simultaneous removal of ammonia nitrogen and recovery of phosphate from swine wastewater by struvite electrochemical precipitation and recycling technology. J. Clean. Prod. 127: 302–310.

Huang, X. L., Y. Chen, and M. Shenker. 2012. Dynamics of phosphorus phytoavailability in soil amended with stabilized sewage sludge materials. Geoderma. 170: 144–153.

Ippolito, J.A., K.A. Barbarick, D.M. Heil, J.P. Chandler, and E.F. Redente. 2003. Phosphorus retention mechanisms of a water treatment residual. J. Environ. Qual. 32: 1857–1864.

Jenkinson, D., and D. Powlson. 1976. The effects of biocidal treatments on metabolism in soil-V: A method for measuring soil biomass. Soil Biol. Biochem. 8: 209–213.

Johnston, A.E., and I. R. Richards. 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. Soil Use Manage. 19: 45–49.

Jupp, A. R., S. Beijer, G.C. Narain, W. Schipper, and J.C. Slootweg. 2021. Phosphorus recovery and recycling–closing the loop. Chem Soc Rev. 50(1): 87–101.

Kannan, A. D., and P. Parameswaran. 2021. Ammonia adsorption and recovery from swine wastewater permeate using naturally occurring clinoptilolite. J. Water Process. Eng. 43: 102234.

Kannan, A. D., J. Dillavou, K. H.H. Gamage, E. Randig, G. M. Hettiarachchi, and P. Parameswaran. 2023. Recovery of high-quality calcium phosphate fertilizer products from anaerobic membrane bioreactor treated swine wastewater. J. Chem. Eng. 453(1): 139539. https://doi.org/10.1016/j.cej.2022.139539

Khatiwada, R., G.M. Hettiarachchi, D. Mengel, and M. Fei. 2012. Speciation of Phosphorus in a Fertilized Reduced Till Soil System: In-Field Treatment Incubation Study. Soil Sci. Soc. Am. J. 76: 2006-2018.

Kilmer, V.J., and L.T. Alexander. 1949. Methods of making mechanical analyses of soils. Soil Sci. 68: 15–24.

Klug, H.P. and L. E. Alexander. 1974. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. John Wiley & Sons, New York.

Kruse, J., and P. Leinweber. 2008. Phosphorus in sequentially extracted fen peat soils: A K-edge X-ray absorption near-edge structure (XANES) spectroscopy study. J. Plant Nutr. and Soil Sci. 171: 613-620.

Lawton, K., and J.A. Vomocil. 1954. The dissolution and migration of phosphorus from granular superphosphate in some Michigan soils. Soil Sci. Soc. Am. Proc. 18: 26–32.

Le Corre, K.S., E. Valsami-Jones, P. Hobbs, S.A. Parsons. 2005. Impact of calcium on struvite crystal size, shape, and purity. J. Cryst. Growth. 283: 514–522.

Le Corre, K.S., E. Valsami-Jones, P. Hobbs, S.A. Parsons. 2007. Impact of reactor operation on success of struvite precipitation from synthetic liquors. Environ. Technol. 28: 1245–1256.

Le, V.G., D.V. Vo, N.H. Nguyen, Y.J. Shih, C.T. Vu, C.H. Liao, Y.H. Huang. 2021. Struvite recovery from swine wastewater using fluidized-bed homogeneous granulation process. J. Environ. Chem. Eng. 9(3).

Lei, Y., B. Song, R.D. van der Weijden, M. Saakes, and C.J.N. Buisman. 2017. Electrochemical Induced Calcium Phosphate Precipitation: Importance of Local pH. Environ. Sci. Technol. 51(19): 11156–11164. https://doi.org/10.1021/acs.est.7b03909

Liao, B.Q., J. T. Kraemer, and D. M. Bagley. 2006. Anaerobic Membrane Bioreactors: Applications and Research Directions. Crit Rev Environ Sci Technol. 36: 489–530.

Lim, K., P.J. Evans, and P. Parameswaran. 2019. Long-Term Performance of a Pilot-Scale Gas-Sparged Anaerobic Membrane Bioreactor under Ambient Temperatures for Holistic Wastewater Treatment. Environ. Sci. Technol. 53(13): 7347–7354. https://doi.org/10.1021/acs.est.8b06198

Lin, H., W. Peng, M. Zhang, J. Chen, H. Hong and Y. Zhang. 2013. A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives. Desalination. 314: 169–188.

Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Liu, R., and R. Lal. 2014. Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (*Glycine max*). Sci Rep. 4: 5686. https://doi.org/10.1038/srep05686

Lombi E., G. M. Hettiarachchi, and K.G. Scheckel. 2011. Advanced in situ spectroscopic techniques and their applications in environmental biogeochemistry: Introduction to the special section. J. Environ. Qual. 40: 659-666.

Lombi, E., K.G. Scheckel, R.D. Armstrong, S. Forrester, J.N. Cutler and D. Paterson. 2006. Speciation and distribution of phosphorus in a fertilized soil: A synchrotron-based investigation. Soil Sci. Soc. Am. J. 70: 2038-2048.

Lombi, E., M.J. McLaughlin, C. Johnston, R.D. Armstrong, and R.E. Holloway. 2005. Mobility, solubility and lability of fluid and granular forms of P fertiliser in calcareous and non-calcareous soils under laboratory conditions. Plant Soil. 269: 25–34.

Lombi, E., M.J. McLaughlin, C. Johnston, R.D. Armstrong, and R.E. Holloway. 2004. Mobility and Lability of phosphorus from granular and fluid Monoammonium phosphate differs in a calcareous soil. Soil Sci. Soc. Am. J. 68: 682–689.

Ma W. Q., L. Ma, J.H. Li, F.H. Wang, I. Sisak, and F.S. Zhang. 2011. Phosphorus flows and use efficiencies and consumption of wheat, rice, and maize in China. Chemosphere. 84: 814–821.

Massey, M., J. Davis, J. Ippolito, and R. Sheffield. 2009. Effectiveness of recovered magnesium phosphates as fertilizers in neutral and slightly alkaline soils. Agron. J. 101: 323–329.

Massey, M.S., 2019. X-ray spectroscopic quantification of Struvite and Dittmarite recovered from wastewater. J. Environ. Qual. 48: 193–198.

Massey, M.S., I. Zohar, J.A. Ippolito, and M.I. Litaor. 2018. Phosphorus sorption to aluminum based water treatment residuals reacted with dairy wastewater: 2. X-ray Absorption Spectroscopy. J. Environ. Qual. 47: 546–553.

Massey, M.S., J.A. Ippolito, J.G. Davis, and R.E. Sheffield. 2010. Macroscopic and microscopic variation in recovered magnesium phosphate materials: implications for phosphorus removal processes and product re-use. Bio resour. Technol. 101: 877–885.

McBeath, T.M., M.J. McLaughlin, J.K. Kirby, and R.D. Armstrong. 2012. Dry soil reduces fertilizer phosphorus and zinc diffusion but not bioavailability. Soil Sci. Soc. Am. J. 76: 1301–1310.

Milani, N., G.M. Hettiarachchi, D.G. Beak, M. J. McLaughlin, J. K. Kirby, and S. P. Stacey. 2015. Fate of zinc oxide nanoparticles coated onto macronutrient fertilizers in an alkaline calcareous soil. PLoS One 10(5): e0126275.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27: 31-36.

Myers, R.G., A.N. Sharpley, S.J. Thien, and G.M. Pierzynski. 2005. Ion-sink phosphorus extraction methods applied on 24 soils from the continental USA. Soil Sci. Soc. Am. J. 69: 511-521.

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. In: D.L. Sparks, A. Page, P. Helmke, R. Loeppert, P. Soltanpour, M. Tabatabai, et al., editors, Methods of soil analysis. Part 3. Chemical methods. ASA, CSSA, SSSA, Madison, WI

Olsen, S.R., and F.S. Watanabe. 1963. Diffusion of phosphorus as related to soil texture and plant uptake. Soil Sci. Soc. Am. J. 27: 648–653.

Omo-Okoro, P.N., C. J. Curtis, K. Pillay. 2023. Importance of phosphorus raw materials in Green Deal strategies, Editor(s): Majeti Narasimha Vara Prasad, Marzena Smol. Sustainable and Circular Management of Resources and Waste Towards a Green Deal. 213-223. https://doi.org/10.1016/B978-0-323-95278-1.00030-9.

Peak, D., J.T. Sims, and D.L. Sparks. 2002. Solid-state speciation of natural and alum-amended poultry litter using XANES spectroscopy. Environ. Sci. Technol. 36: 4253-4261.

Pierzynski, G.M. 1991. The chemistry and mineralogy of phosphorus in excessively fertilized soils. Crit. Rev. Environ. Sci. Technol. 21: 265-295.

Pierzynski, J. and G.M. Hettiarachchi. 2018. Reactions of phosphorus fertilizers with and without a fertilizer enhancer in three acidic soils with high phosphorus-fixing capacity. Soil Sci. Soc. Am. J. 82: 1124-1139.

Ping, Q., Y. Li, X. Wu, L.u. Yang, and L. Wang. 2016. Characterization of morphology and component of struvite pellets crystallized from sludge dewatering liquor: Effects of total suspended solid and phosphate concentrations. J. Hazard. Mater. 310: 261–269.

Qiu, M., A. Singh, D. Wang, J. Qu, M. Swihart, H. Zhang, and P.N. Prasad. 2019. Biocompatible and biodegradable inorganic nanostructures for nanomedicine: Silicon and black phosphorus. Nano Today. 25: 135–155.

Rabinovich, A., A.A. Rouff, B. Lew, M.V. Ramlogan. 2018. Aerated fluidized bed treatment for phosphate recovery from dairy and swine wastewater. ACS Sustain. Chem. Eng. 6 (1): 652–659.

Ravel B., and M. Newville. 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12: 537–541.

Rech, I., P. Withers, D. Jones, and P. Pavinato. 2018. Solubility, diffusion and crop uptake of phosphorus in three different struvites. Sustainability. 11(1): 134.

Roefs, I., Meulman, B., Vreeburg, J.H.G., Spiller, M., 2017. Centralised, decentralised or hybrid sanitation systems? economic evaluation under urban development uncertainty and phased expansion. Water Res. 109: 274–286. https://doi.org/10.1016/j.watres.2016.11.051

Romer, W. 2006. Plant availability of P from recycling products and phosphate fertilizers in a growth-chamber trial with rye seedlings. J. Plant Nutr. Soil Sci. 169: 826–832.

SAS Institute. 2011. The SAS system for Windows version 9.1.3. SAS Institute, Cary, NC.

Schipper, W.J., Klapwijk, A., Potjer, B., Rulkens, W.H., Temmink, B.G., Kiestra, F.D., Lijmbach, A.C.M., 2001. Phosphate recycling in the phosphorus industry. Environ Technol. 22: 1337–1345. https://doi.org/10.1080/09593330.2001.9619173.

Schroder, J. J., A.L. Smit, D. Cordell, and A. Rosemarin. 2011. Improved phosphorus use efficiency in agriculture: A key requirement for its sustainable use. Chemosphere. 84: 822–831.

Sengupta, S. and A. Pandit. 2011. Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer. Water Res. 45: 3318-3330.

Sharpley, A., H.P. Jarvie, A. Buda, L. May, B. Spears, and P. Kleinman. 2013. Phosphorus legacy: Overcoming the effects of past management practices to mitigate future water quality impairment. J. Environ. Qual. 42: 1308-1326

Shin, J. H., S. M. Lee, Y. J. Jung, C. Y. Chung, and H. S. Noh. 2005. Enhanced COD and nitrogen removals for the treatment of swine wastewater by combining submerged membrane bioreactor (MBR) and anaerobic upflow bed filter (AUBF) reactor. Process Biochem. 40: 3769–3776.

Smil, V. 1999. Nitrogen in crop production: An account of global flows. Global Biogeochem. Cycles. 13: 647-662.

Soil Survey Laboratory Staff. 2004. Soil survey methods manual. Soil survey investigations Rep. No. 42 Version 4.0. National Soil Survey Center, Lincoln, NE.

Soil Survey Staff. 2011. Soil Survey Laboratory Information Manual. Soil Survey Investigations. Report No. 45, Version 2.0. R. Burt (ed.) U.S. Department of Agriculture, Natural Resources Conservation Service.

Speiser, C., T. Baumann, and R. Niessner. 2001. Characterization of municipal solid waste incineration (MSWI) bottom ash by scanning electron microscopy and quantitative energy dispersive X-ray microanalysis (SEM/EDX). Fresenius J Anal Chem. 370 :752–759.

Sposito, G. 1989. The Chemistry of Soils. xiii 277 pp. New York, Oxford: Oxford University Press. ISBN 0 19 504615 3.

Stoop, W.A. 1983. Phosphate adsorption mechanisms in Oxidic soils: Implications for P-availability to plants. Geoderma 31: 57-69.

Stratful, I., M.D. Scrimshaw, and J.N. Lester. 2001. Conditions influencing the precipitation of magnesium ammonium phosphate. Water Res. 35: 4191–4199.

Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima, and Y. Fukumoto. 2005. Recovery of phosphorus from swine wastewater through crystallization. Bioresour. Technol. 96: 1544–1550.

Syers, J. K., A.E. Johnston, and D. Curtin. 2008. Efficiency of Soil and Fertilizer Phosphorus Use. FAO Fertilizer and Plant Nutrition Bulletin. FAO, Rome.

Szogi, A. A., M.B. Vanotti, and P.D. Shumaker. 2018. Economic recovery of calcium phosphates from swine lagoon sludge using Quick Wash process and geotextile filtration. Front. sustain. food syst. 2: 37.

Szogi, A.A., P.J. Bauer, and M.B. Vanotti. 2012. Vertical distribution of phosphorus in a sandy soil fertilized with recovered manure phosphates. J. Soil Sediments. 12: 334-340.

Talboys, P.J., J. Heppell, T. Roose, J.R. Healey, D.L. Jones, and P.J.A. Withers. 2016. Struvite: a slow-release fertilizer for sustainable phosphorus management. Plant Soil. 401: 109-123

Tilman, D., K.G. Cassman, P.A. Matson, R. Naylor, and S. Polask. 2002. Agricultural sustainability and intensive production practices, Nature. 418(6898): 671–677.

Tran, A. T. K., Y. Zhang, D. De Corte, J.B. Hannes, W. Ye, P. Mondal, N. Jullok, B. Meesschaert, L. Pinoy, and B. Van der Bruggen. 2014. P-recovery as calcium phosphate from wastewater using an integrated selectrodialysis/crystallization process. J. Clean. Prod. 77: 140–151. https://doi.org/10.1016/j.jclepro.2014.01.069

USEPA. 2007. Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils and oils. Test methods. USEPA. http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3051a.pdf

Valsami-Jones, E., 2001. Mineralogical controls on phosphorus recovery from wastewaters. Mineral. Mag. 65: 611–620.

Vance, C.P. 2001. Symbiotic nitrogen fixation and phosphorus acquisition. Plant nutrition in a world of declining renewable resources. Plant Physiol. 127:390-397.

Vasenko, L., and H. Qu. 2017. Effect of NH4-N/P and Ca/P molar ratios on the reactive crystallization of calcium phosphates for phosphorus recovery from wastewater. J. Cryst. Growth. 459: 61–66.

Vogel, T., J. Kruse, N. Siebers, M. Nelles, and B. E. Löbermann. 2017. Recycled Products from Municipal Wastewater: Composition and Effects on Phosphorus Mobility in a Sandy Soil. J. Environ. Qual. 46: 443–451.

Wang, J., J.G. Burken, X. Zhang, R. Surampalli. 2005. Engineered struvite precipitation: impacts of component-ion molar ratios and pH. J. Environ. Eng. 131: 1433–1440.

Wang, L., and G.H. Nancollas. 2008. Calcium Orthophosphates: Crystallization and Dissolution. Chem. Rev. 108(11): 4628–4669. https://doi.org/10.1021/cr0782574

Watson, M.E., and J.R. Brown. 1998. pH and lime requirement. In: J.R. Brown, editor, Recommended chemical soil test procedures for the north central region. Missouri Agric. Exp. Stn, Univ. of Missouri, Columbia, MO. 13–16.

Weeks, J.J., and G.M. Hettiarachchi. 2020. Source and formulation matter: new insights into phosphorus fertilizer fate and transport in mildly calcareous soils. Soil Sci. Soc. Am. J. 84: 731–746.

Werner, F. and J. Prietzel. 2015. Standard protocol and quality assessment of soil phosphorus speciation by P K-edge XANES spectroscopy. Environ. Sci. Technol. 49: 10521-10528.

Wu, Q., and P.L. Bishop. 2004. Enhancing struvite crystallization from anaerobic supernatant. J. Environ. Eng. Sci. 3: 21–29.

Yan, Z., S. Chen, J. Li, A. Alva, and Q. Chen. 2016. Manure and nitrogen application enhances soil phosphorus mobility in calcareous soil in greenhouses. J. Environ. Manage. 181: 26-35.

Zarcinas, B.A., M.J. McLaughlin, and M.K. Smart. 1996. The effect of acid digestion technique on the performance of nebulization systems used in inductively coupled plasma spectrometry. Commun. Soil Sci. Plant Anal. 27: 1331–1354.

Zhang, X. D., H. Spanjers, J.B. van Lier. 2013. Potentials and limitations of biomethane and phosphorus recovery from sludges of brackish/marine aquaculture recirculation systems: A review. J Environ Manage. 131: 44–54.

Zhou, Z., D. Hu, W. Ren, Y. Zhao, L.M. Jiang, and L. Wang. 2015. Effect of humic substances on phosphorus removal by struvite precipitation. Chemosphere. 141: 94–99.

Zohar, I., M.S. Massey, J.A. Ippolito, and M.I. Litaor. 2018. Phosphorus sorption to aluminum-based water treatment residuals reacted with dairy wastewater: 1. Isotherms, XRD, and SEM-EDS analysis. J. Environ. Qual. 47: 538–545.

Chapter 6 - Implications of management practices on sediment and soil phosphorus speciation in no-till corn and soybean rotation

Abstract

A crucial contributor to decreased surface water quality is the loss of phosphorus (P) from non-point agricultural sources. Agricultural runoff often contains P in both dissolved and sediment-bound forms. Although not readily available, sediment P can contribute to eutrophication upon transformation to bioavailable P. No-till and cover cropping conservation practices have been recommended for reducing erosion and nutrient loss from cropping systems. The overall aims of this study were to characterize and evaluate the effects of five-year-long fertilizer (placement and source) and cover crop management on P speciation in surface runoff sediments and source soil (0- 2.5cm) collected from Kansas Agricultural Watershed (KAW) field laboratory Manhattan, Kansas. In 2014, this field-scale experiment was established in a no-till, corn-soybean cropping system in 2×3 full factorial with 18 0.5-ha watersheds in a randomized complete block design. There were two cover crop treatments (with and without a winter crop) and three P fertilizer management treatments (no P, fall broadcast diammonium phosphate, and spring subsurface injected ammonium polyphosphate). To evaluate the efforts from the five-year long study, P fractionation in sediment samples collected throughout 2020 and the source soil collected in 2019 fall were analyzed using a modified sequential P extraction (SEDEX) method. The direct P speciation was done using X-ray absorption near edge structure spectroscopy (XANES). The indirect P speciation (fractionation) results showed that the management practices affected the exchangeable, organic-associated, and iron-bound P fractions in sediments and the exchangeable and residual fractions in source soil. Direct P speciation results showed that the iron-associated P was greater in no cover crop treatment, and clay-adsorbed P was

greater in cover crop treatment in both sediment and soil. Clay adsorbed P was higher in spring-injected treatments in soil. These results suggest that management practices differently affected iron-associated and other P species. Developing P fertilizer and cropping system management options with a clear understanding of soil P transformations helps maintain environmental sustainability.

Introduction

Phosphorus (P) is a vital crop nutrient, and crop producers worldwide apply P-based fertilizers for optimum yield. However, agricultural production has been identified as a significant source of sediment, nitrogen, and P pollution, leading to surface water quality issues (Sharpley & Tunney, 2000). The increase in P pollution to surface water is especially detrimental, although not exclusive, to freshwater bodies (Moody, 2011). Eutrophication and associated harmful algal blooms are conservatively estimated to cost the United States economy 2.4-4.6 billion dollars a year (Dodds et al., 2009). In addition to severe economic impact, harmful algal blooms increase the risk of adverse health impacts on humans and animals (Hudnell, 2010). The linkage between non-point agricultural P pollution and the degradation of surface water quality leads to creating agricultural best management practices (BMP) to reduce P loss. Therefore, to address environmental concerns such as erosion, nutrient loss, and water pollution, the United States Department of Agriculture Natural Resources Conservation Service (USDA-NRCS) promotes conservation practices designed to reduce erosion and pollution while improving soil health, which includes changes in tillage practices and planting cover crops (NRCS, 2015).

In multiple ecoregions around the globe, no-till has been shown to reduce sediment in the runoff by up to 80% (Smith et al., 2015; TerAvest et al., 2015). Cover crops have been shown to further reduce erosion by increasing surface plant biomass, improving aggregate stability by increasing soil organic matter in the soil profile, and increasing macropores from their root growth (Eichler-Löbermann et al., 2008; Blanco-Canqui et al., 2011). Cover crops can successfully disrupt P transportation routes, lessen erosion losses, and enhance water infiltration (Blanco-Canqui et al., 2011; Loss et al., 2015; Ruffati et al., 2019; Blanco-Canqui & Ruis,

2020). It is important to note that cover crops' efficacy in mitigating total and dissolved P losses may differ across various studies (Christianson et al., 2017; Baulch et al., 2019; Macrae et al., 2021). Therefore, gathering more information about the interactions between cover crops and P fertilizer management is crucial to developing new agricultural BMPs.

Phosphorus can be found in dissolved or sediment-bound forms in agricultural runoff. The dissolved P is mainly in orthophosphate, the main bioavailable form of P (Machesky et al., 2010). Sediment P is sorbed into clays, calcium carbonate, crystalline and amorphous hydrous iron, aluminum oxides, and organic material in surface runoff (Machesky et al., 2010). Although not readily available, sediment P helps to maintain and control dissolved P. Therefore, it may contribute to continued eutrophication. The P concentration in surface flow is often observed to relate to fertilization rates, P cycling in the plant-soil system, and the amount of labile P in soils. Therefore, finding ways to mitigate these P losses from agricultural runoff is essential.

One commonly adopted method of identifying P species in sediment is the fractionation approach. The SEDEX (sedimentary extraction) procedure of Ruttenberg, 1992 is one of the more thoroughly developed and tested chemical extraction schemes for sedimentary analysis. The SEDEX method separates sediment P into five operationally defined pools. However, it suffers from intrinsic limitations such as artifacts associated with reagent selectivity and the inability to differentiate specific solid-state P forms (e.g., amorphous versus crystalline mineral P phases) (Li et al., 2015). In recent years, advanced spectroscopic techniques such as X-ray absorption near edge structure spectroscopy (XANES) have been increasingly applied to complement the SEDEX and other extraction methods (Kizewski et al., 2011; Liu et al., 2013; Li et al., 2015). The P K-edge XANES are nondestructive, element-specific techniques that can probe the local molecular bonding environment around P atoms and thereby can be used to

determine P species (Peak et al., 2002; Kar et al., 2011). In summary, individual techniques have certain limitations, but a combination of complementary techniques enhances species identification with less uncertainty (Hettiarachchi et al., 2008; Lombi et al., 2011; Milani et al., 2015) and has been used successfully in different environments (Li et al., 2015).

A previous study conducted during the first five years of the same study field by Carver et al., 2022, showed that the spring-injected P fertilizer treatment had 19% less total P and 33% less dissolved reactive P (DRP) loss than the fall broadcast treatment. In addition, cover crops showed an inconsistent effect on total P loss, and it was related to cover crop effects on sediment loss. However, cover crops showed a clear and consistent impact on DRP concentrations and loads in the runoff. Cover crops increased the DRP loss in three out of four years of the first five years of the study. In the years with high sediment loss, the harvest year 2019, the cover crop treatment decreased total P loss by reducing potential particulate P loss associated with erosion. Further, the findings of that study suggested that proper fertilizer management is vital to prevent nutrient loss and protect water quality and cover crops can be used to reduce P loss from erosion-prone areas. Therefore, this current study was designed to further understand how the P speciation in sediments and source soil is affected by the P management practices and cover crops. We hypothesize that the speciation and solubility of sediment and source soil P vary with P fertilizer source, application method or time of application, and presence or absence of cover crops. The objectives of this study were to characterize and evaluate the effects of a five-year-long fertilizer (placement and source) and cover crop management on P speciation in surface runoff sediments from natural precipitation events and source soil (0- 2.5cm) collected from Kansas Agricultural Watershed (KAW) field laboratory Manhattan, Kansas under no-till corn (*Zea mays* L.)-soybean (*Glycine max* L.) rotation.

Materials and Methods

Field site

This study was conducted at the Kansas Agricultural Watershed (KAW) field laboratory located near Manhattan, Kansas. This study had eighteen small-scale watersheds (i.e., plots), which were around 0.5 ha in size. Each plot had a 0.46 m high H-flume and automated water sampler (ISCO Teledyne 6700 or 6712 series with a 730 bubbler unit, Lincoln, NE). The plots were separated from each other with berms and terraces. The soil type was Smolan and related series (Fine, smectitic, mesic Pachic Argiustolls) with silt loam to silty clay loam surface texture with a 3–7% slope. The site has been in a continuous no-till, corn-soybean rotation since its establishment in 2014.

Experimental design

This study was organized in a 2x3 complete factorial treatment design arranged in a randomized complete block design (blocked by landscape position). There were three levels of P management: no P fertilizer control (CN); fall surface broadcast diammonium phosphate (DAP, 61 kg P_2O_5 ha^{-1}, FB), spring subsurface injected ammonium polyphosphate (SI, 61 kg P_2O_5 ha^{-1}, SI) and two levels of cover crop management: no cover (NC) and with cover crop (CC). The KAW field laboratory map is given in Figure 1. Cover crops have been planted annually since 2015, including winter wheat (2015), triticale, and rapeseed (2016, 2017), winter wheat and rapeseed (2018). Further agricultural management details can be found in Caver et al., 2022.

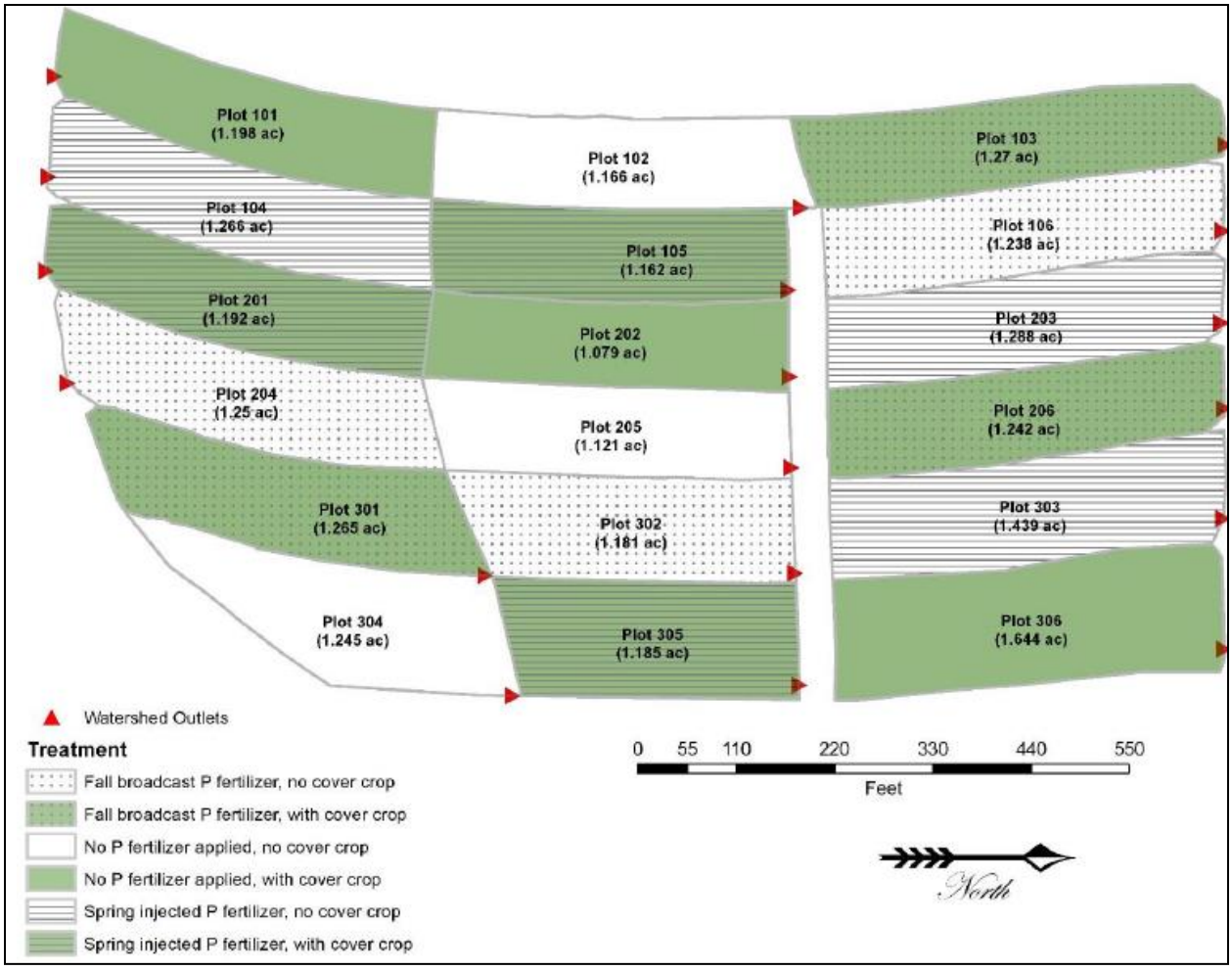


Figure 6.1. Kansas Agricultural Watershed (KAW) Field Laboratory Map

Sediment sample collection and processing

The surface runoff samples were collected from each plot in 2020 after every natural precipitation event. In order to collect the runoff samples, a 200-mL sample was collected for every 1 mm surface runoff and composited in a 10 L Nalgene carboy. The runoff samples were removed from the field within 24 h after runoff and stored at 4°C until further processing. Then the runoff samples were centrifuged for 20 min at 10000 rpm, and the sediments were collected and freeze-dried. Due to the low quantities of sediments available for analysis, they were

combined, and further analysis was done for three durations as duration 1, 2, and 3 (A detailed outline for the runoff events is given in Supporting information Figure 6.9).

Soil sample collection and processing

Soil samples were collected from three geo-referenced subplot locations within each plot from 0-2.5 cm depth in October 2019. All soil samples were air-dried and ground to pass through a 2 mm sieve. Three replicates were analyzed separately.

Sequential extraction

Phosphorus fractionation in sediments for three durations and source soil were evaluated using a modification (Baldwin, 1996) of the SEDEX extraction scheme (Ruttenberg, 1992). The modification incorporates an additional 16 h, 1*M* $NaHCO_3$ step (P_{Hum}) after the P_{Ex} step to differentiate organic matter-associated P, which may otherwise be co-extracted during the P_{Fe} step. Briefly, 0.2 g ± 0.005 of sediment or soil were weighed into 50 mL centrifuge tubes, and the solid-to-solution ratio was maintained at 1:100. Then, the sediment or soil was sequentially exposed to a series of solutions intended to target specific P species (Table 6.1). The same sequential extraction procedure was used for sediment and source soil to compare the P fractionation. All samples were centrifuged after extraction at 2000 rpm for 10 minutes and filtered through Whatman No. 42 filter papers (GE Healthcare Bio-Sciences, Pittsburgh, PA). Samples were washed with 20 ml of 1*M* $MgCl_2$ between extractions, except after the first MQ water was used. The first two step samples (P_{Ex} and P_{Hum}) were quantified colorimetrically using a Beckman-Coulter DU-800 spectrophotometer (Brea, CA) (Murphy & Riley, 1962), and the rest of the steps were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, 720-ES, Varian, Santa Clara, CA). The supernatants of steps one and two were separately digested by combining 2.5 mL of solution with 500 μL sulfuric acid and heating to

100°C for one hour. Samples were analyzed using Murphy & Riley, 1962 to determine "Other P" in each section by comparing pre- and post-digestion. The "Other P" results between replicates were highly variable, possibly due to polyphosphate hydrolysis post-extraction, and were thus deemed too unreliable to be presented.

Table 6.1. Summary of the modified SEDEX sequential extraction protocol used on sediment and source soil samples.

Extractant and condition	Targeted P fraction
1*M* $MgCl_2$ pH 8 for 2 h at 25 °C	Exchangeable or loosely sorbed P (P_{Ex})
1*M* $NaHCO_3$ pH 7.6 for 16 h at 25 °C	Organic associated P (P_{Hum})
0.3*M* Sodium citrate with 1M $NaHCO_3$ pH 7.6 for 8 h at 25 °C with 1.125 g of Na dithionite (CDB)	Fe-bound P (P_{Fe})
1*M* Na acetate with acetic acid pH 4 for 6 h at 25 °C	Authigenic carbonate fluorapatite plus biogenic apatite plus $CaCO_3$-bound P (P_{Ca})
1*M* HCl 16 h at 25 °C	Detrital apatite plus other inorganic P (P_{De})
1*M* HCl 16 h after ashing at 550 °C at 25 °C	Residual P* (P_{Re})

*Soil residual P was calculated by subtracting the summation of P in step 1-5 from total P

Synchrotron analysis

The X-ray absorption near-edge structure spectroscopy analysis was only performed for the duration 1 and 3 sediment samples and soil samples. The P K-edge XANES data were collected at Sector 9-BM-B, Advanced Photon Source, Argonne National Laboratory, Argonne, IL. All spectra, including the P_2O_5 standard used for energy calibration, were collected with a solid-state drift detector in fluorescence mode. A 7-mm sediment/soil pellet was prepared with the KBr Quick Press Kit (International Crystal Laboratories, Garfield, NJ) and mounted carefully on the sample holder with double-sided carbon tape (SPI Supplies, West Chester, PA) and placed into a helium filled chamber for analysis. Four and three scans were collected per sediment and source soil sample respectively at a range of 2.1 to 2.4 keV.

Background correction and linear combination fitting of the experimental spectra were completed in Athena (v.0.9.25) (Ravel & Newville, 2005) according to the concepts set forth by Werner & Prietzel, 2015. Previously collected P reference standards were also used, and the P_2O_5 standard spectra were collected during each run for spectral alignment. Briefly, three or four scans were merged to limit noise. Pre-edge and normalization ranges were not fixed, allowing for each sample's maximized fit. All spectra were adjusted such that E_0 of 2149 eV corresponded to one-half the height of the white line peak. Reference spectra were eliminated if they comprised <5% of the calculated composition and the fitting was repeated.

Statistical analysis

All sediment and soil data from sequential extraction were analyzed in SAS (SAS Institute, 2011) through the Proc MIXED procedure. The two levels of cover crop management and three levels of P fertilizer management were arranged in a 2 x 3 factorial treatment structure

in randomized complete block design. Tukey's HSD test was used to compare all treatments at a $p = 0.05$ level of significance.

Results and Discussion

Sequential extraction of P pools – Soils and sediments

Overall, the sequential extraction results showed that the P and cover crop management affected the exchangeable (P_{Ex}), organic associated (P_{Hum}), and iron-bound P (P_{Fe}) fractions in sediments and exchangeable (P_{Ex}) and residual fractions (P_{Re}) in source soil (Supporting information Table 6.2 & 6.3). Previous studies conducted during the first five years of this study filed showed that the SI method of applying P fertilizer resulted in significantly smaller concentrations and loads of both total P and DRP compared to the FB treatment (Carver et al., 2022). Further they showed relatively consistent trends over time, there was a significant main effect of P fertilizer management practice on concentrations and loads of both total P and DRP. In this current study which was conducted at the end of first five years the P_{Ex} fraction in source soil also showed a significant difference by P treatment (Figure 6.2a), and in sediments by both P treatment and cover crop in all three durations (Figure 6.2b & 6.2c). In both source soil and sediments, FB showed the highest P_{Ex} (Figure 6.2a & 6.2b). Differences in the application method are likely to result in this. The FB was a surface application, and there was not much soil to react with, and the spring injected was a subsurface application that could go into the soil and react. Also, FB was applied as a granular fertilizer DAP, and SI was applied as a liquid fertilizer APP, which facilitates diffusion of P into a larger soil volume, and therefore, more retention in soil. In literature, it is well documented that the application of P-containing fertilizers increased P loss compared to no P fertilizer controls depending on the timing of runoff and soil conditions at the time of fertilizer application (Torbert et al., 1999; Smith et al., 2004a, 2004b, 2007; Li et al.,

2020). In no-till management, P fertilizer is often broadcast on the soil surface, concentrating the nutrient in the top few mm of soil due to the lack of mechanical incorporation, where surface water interacts most (Sims et al., 2000). Subsurface placement of P fertilizer is a well-recognized management practice that can reduce the risk of P loss in runoff and minimize nutrient loss (Sharpley et al., 1992; Pote et al., 2006; Smith et al., 2016). Smith et al., 2016 also found that injecting liquid polyphosphate fertilizer had less soluble and total P loss than annual and biannual surface broadcasting in no-till fields. Incorporating P fertilizer decreased the average total P concentration in the runoff between 90 and 99% compared to surface-broadcast P fertilizer application (Pote et al., 2006). Smith et al., 2016 further found that the subsurface placement of P fertilizer also decreased the total P load in the runoff by approximately 97% compared to surface-broadcast P fertilizer application.

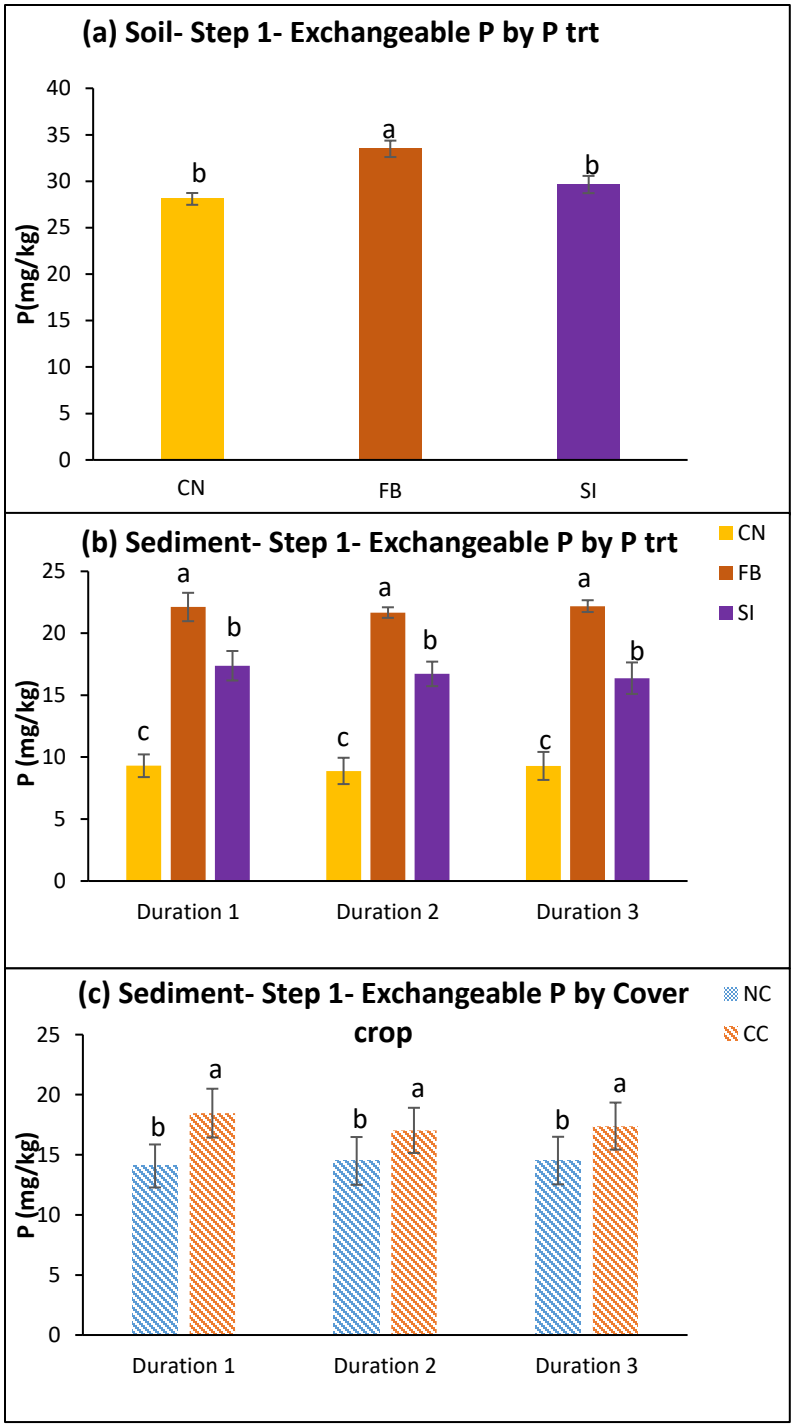


Figure 6.2. (a) The Exchangeable P (P_{Ex}) fraction in source soil by P treatment. (b) The P_{Ex} fraction in sediments by P treatment in all three durations. (c) The P_{Ex} fraction in sediments by cover crop in all three durations. Means within a treatment containing the same letter are not significantly different at $p = 0.05$ according to Tukey's pairwise method. CN, control; FB, fall broadcast; SI, spring injection; CC, with cover crops; NC, no cover crops.

Carver et al., 2022 also showed that the addition of a cover crop had an inconsistent effect on total P loss, with no effect in 2016 and 2017, increasing loss in 2018 by 56%, and decreasing it in 2019 by 40% during the first five years of the study and they showed that the inconsistent impact of cover crops on total P loss was related to cover crop effects on sediment loss. In the current study the P_{Ex} fraction was higher in the CC treatment than in the NC in sediments (Figure 6.2c). Root exudates/organic acids by cover crops alter soil's P sorption capacity. These mechanisms include ligand promoted dissolution or the enhanced dissolution via complexation and organic acid competition for the adsorption sites and ultimately less or weak sorption of P in soils. Cover crops have shown the capability to access and solubilize more recalcitrant forms of soil P through the exudation of P solubilizing compounds, the release of organic P mineralizing compounds, and by modifying the rhizospheric microbial population (Hallama et al., 2019). Cover crops can also modify forms of P present in the soil and may lead to competitive adsorption (Violante & Gianfreda, 1993). Additionally, adding a cover crop demonstrated increased microbial biomass and elevated total C concentration, leading to increased mineralization of recalcitrant forms of P in the soil (Starr, 2021). Furthermore, cover crops also showed a greater capacity to move P to the soil surface and access traditionally non-available P fractions via the establishment of symbiotic relationships with mycorrhizal fungi and secretion of P solubilizing root exudates or alteration of root architecture (Hallama et al., 2019). Dube et al., 2014 and Wang et al., 2021 also found that adding a cover crop increases the concentration of total P in surface soils.

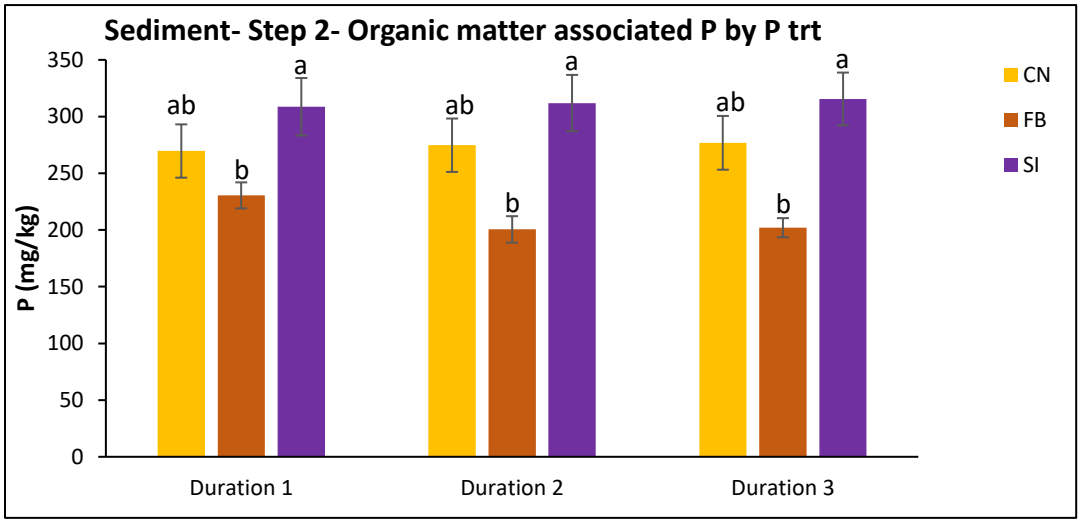


Figure 6.3. The organic matter associated P (P_{Hum}) fraction in sediments by P treatment in all three durations. Means within a treatment containing the same letter are not significantly different at $p = 0.05$ according to Tukey's pairwise method. CN, control; FB, fall broadcast; SI, spring injection.

The P_{Hum} fraction showed a significant difference only by the P treatment in sediments in all three durations. There was a clear separation between FB and SI in the P_{Hum} fraction, with no difference between CN and FB or control and SI (Figure 6.3). The differences in the source of P as DAP or APP can cause this. Besides, regarding this second step, part of the loosely bound organic associated P could have already been extracted in Step 1. While each subsequent extraction in this series is intended to target specific and increasingly recalcitrant P species, these fractions are operationally defined by the reagents used. Each fraction may represent several P chemical forms that all happen to be extracted by the same procedural steps, which makes interpretation challenging. This fraction is a modification of the SEDEX extraction scheme that Baldwin, 1996 proposed to differentiate organic matter-associated P, which may otherwise be co-extracted during the P_{Fe} step.

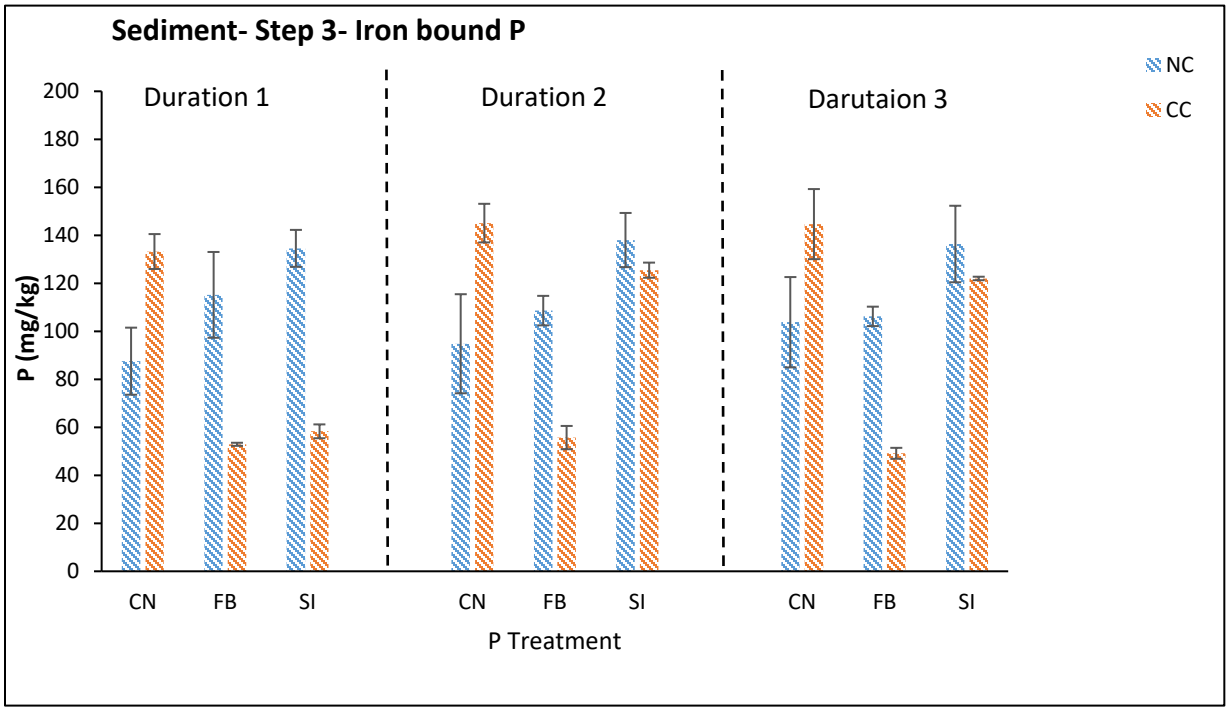


Figure 6.4. The iron bound P (P_{Fe}) fraction in sediments by P treatment in all three durations. Only duration 1 showed significant interaction at p = 0.05. CN, control; FB, fall broadcast; SI, spring injection; CC, with cover crops; NC, no cover crops.

The P_{Fe} fraction showed a significant difference only by the P treatment in the first duration in sediments. Iron-bound P was affected differently in control vs. P treatments (Figure 6.4). It showed an increase in CN with cover crops compared to no cover crops and a decrease in FB with cover crops compared to no cover crops. That suggests that the reaction pathways for native P and the added P are different in these sediments. This also suggests that cover crop enhance the preservation of Fe-bound P or transformation of Fe-bound P to non-erodible P. Most P extracted within the P_{Fe} fraction was co-precipitated with iron (III) oxyhydroxides, that were reductively dissolved by dithionite (Ruttenberg, 1992). The extent of dissolution of Fe (III) minerals depends on the redox condition, sediment composition (phyllosilicates vs. oxides), and degree of crystallinity (amorphous vs. crystalline), among other factors (Li et al., 2015).

Adding P fertilizer in both FB and SI treatments increased P_{Res} and total P concentrations near the soil surface compared to CN, but no significant differences were observed between the FB and SI treatments (Figure 6.5). Surprisingly, there is a lack of difference between the FB and SI treatments because the SI treatment is a subsurface placement of P, and within the soil system, there is inherent immobility of P, which suggests that in the no-till system, subsurface placement may not reduce the potentially greater near-surface concentrations of P. Lack of difference in P_{Res} and total P between the FB and SI treatment could be attributed to inconsistencies in the placement depth of P fertilizer applied in the SI treatment. The SI treatment may not always be placed at 5 cm below and to the side of the seed at planting, leading to variability in results. Additionally, plant uptake followed by deposition and decomposition of residue could lead to rapid cycling of P to the soil surface and contribute to this lack of difference. Insufficient vertical mixing of soil and crop residue may lead to higher concentrations of dissolved P in surface runoff in the CN treatment (Bordoli & Mallarino, 1998). Daryanto et al., 2017 found that dissolved P in surface runoff in no-till systems is 35% greater than in conventionally tilled systems.

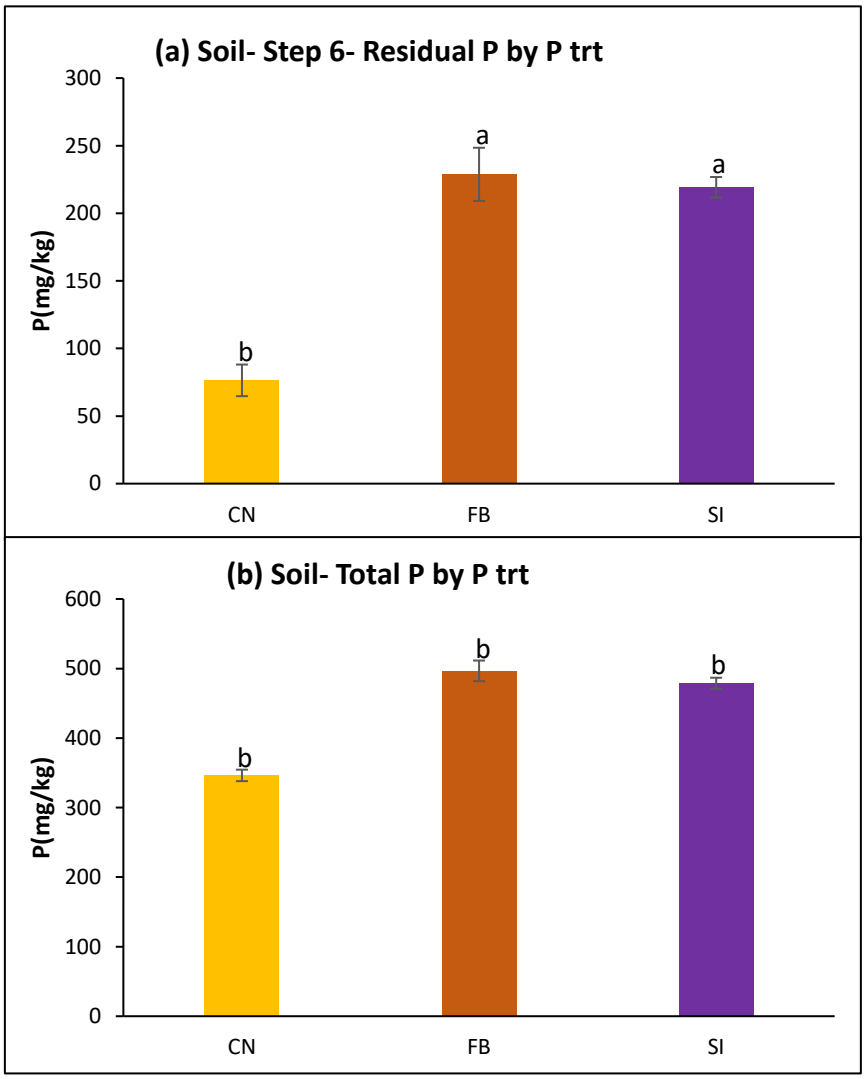


Figure 6.5. (a) The residual P (P_{Res}) fraction in source soil by P treatment. (b) The total P in source soil by P treatment. Means within a treatment containing the same letter are not significantly different at p = 0.05 according to Tukey's pairwise method. CN, control; FB, fall broadcast; SI, spring injection.

Phosphorus XANES- Soils and Sediments

The XANES technique allows the determination of the oxidation state and an element's local chemical and structural environment (Fendorf & Sparks, 1996), enabling speciation. The speciation of contaminants and nutrients in soils significantly determines their availability and fate in the environment. This technique has been widely used for the speciation of organic and inorganic P in soils, sediments, agricultural byproducts and fertilized soils (Hesterberg et al., 1999; Peak et al., 2002; Khatiwada et al., 2011; Lombi et al., 2006; Ajiboye et al., 2008; Kruse & Leinweber, 2008; Weeks & Hettiarachchi, 2020).

The control soil was dominated by the Fe-bound P species followed by apatite like P and clay- Al- adsorbed P species, whereas the P added soil were dominated by clay- Al- adsorbed P species (Figure 6.6). This suggests that the added P has contributed to change in P speciation in control soil. Total P differences obtained by the sequential extraction for source soil also showed the difference between control and P added soils. In addition, when comparing the soil without cover crop treatments, it was also dominated by Fe-bound P species, whereas the cover crop treatments were dominated by the clay-Al- adsorbed P species (Figure 6.6). This suggests that the cover crop treatment enhanced the clay-Al adsorbed P at the expense of the Fe-bound P. In sediments, a similar trend was observed in cover and no cover crop treatments where no cover crop treatment dominated by the Fe-bound P species, and the cover crop treatments dominated by the clay-Al- adsorbed P species (Figures 6.7 & 6.8). This also suggests that cover crop treatment transforms Fe-bound P to other P. In other ways, cover crop treatment redistributes the P species in this cropping system. This could be due to cover crops changing the iron chemistry in surface soil via ligand-promoted dissolution by root exudates and competitive adsorption by

organic acids (Johnson & Loeppert, 2006). The sequential extraction P_{Fe} results also showed a similar trend, which could be the reason for the reduced solubility of P in cover crop treatments. Also as expected from the sequential extraction step P_{Ex}, cover crop treatment showed more exchangeable P than no cover crop treatments. In sediments SI treatment showed higher Fe-bound P species than the FB treatment (Figures 6.7 & 6.8), which could lead to less solubility of P in SI treatment. A study conducted by Wang et al., 2021, showed that 14 years of white clover (*Trifolium repens* L.) and orchard grass (*Dactylis glomerata* L.) cover crops in a rain-fed apple orchard on the Weibei Loess Plateau, China enhanced the bioavailability of soil P by increasing the contents of total P, microbial P, organic P and certain forms of inorganic P (e.g. Al-P, Ca-P and Fe-P) in the surface soil.

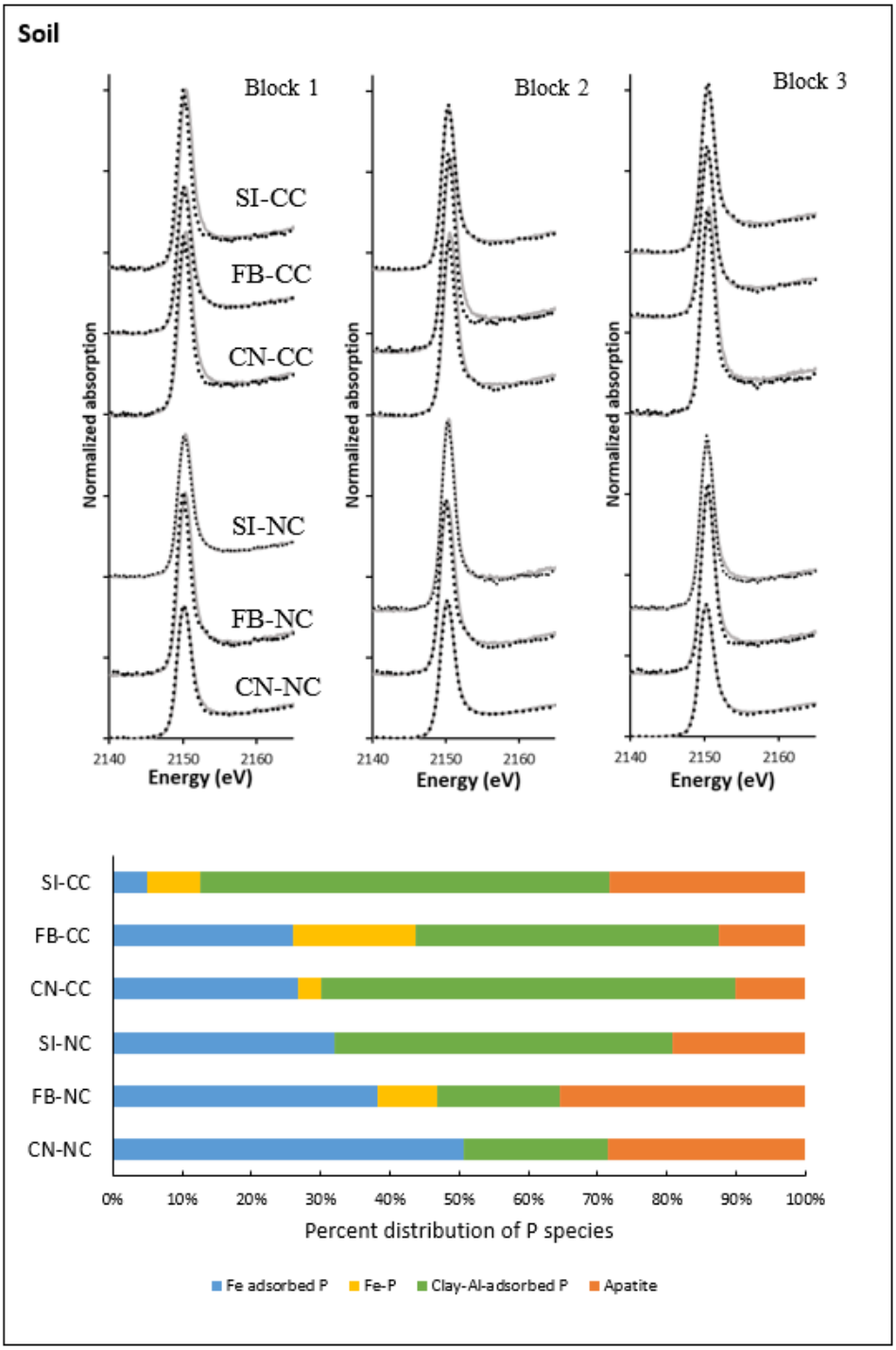


Figure 6.6. Normalized P K-edge X-ray absorption near edge structure spectra of soil with results of linear combination fitting as percent distribution of P species. CN-NC, control-no cover crops; FB-NC, fall broadcast-no cover crops; SI-NC, spring injection-no cover crops; CN-CC, control-with cover crops; FB-CC, fall broadcast-with cover crops; SI-CC, spring injection-with cover crops.

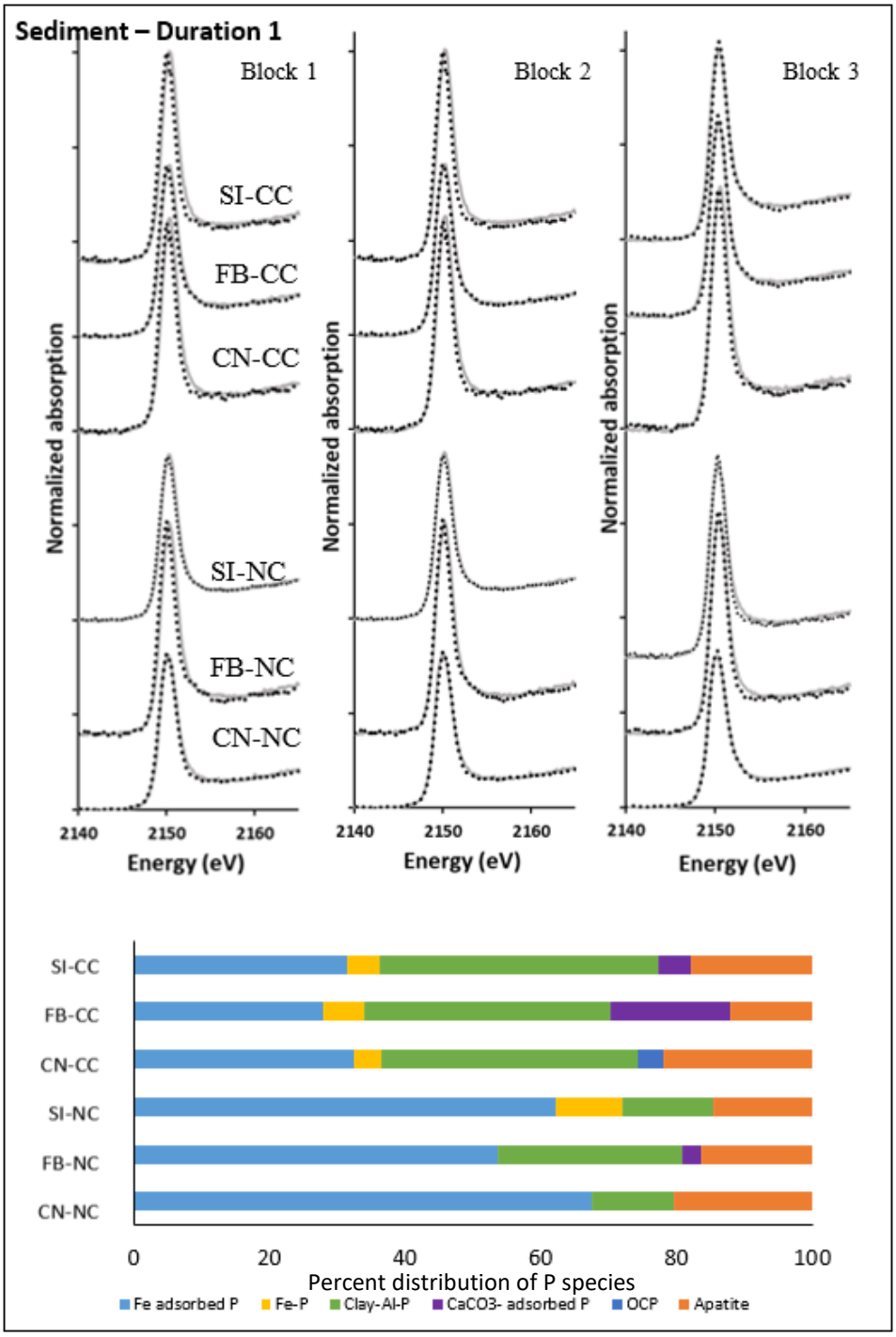


Figure 6.7. Normalized P K-edge X-ray absorption near edge structure spectra of sediment duration 1 with results of linear combination fitting as percent distribution of P species. CN-NC, control-no cover crops; FB-NC, fall broadcast-no cover crops; SI-NC, spring injection-no cover crops; CN-CC, control-with cover crops; FB-CC, fall broadcast-with cover crops; SI-CC, spring injection-with cover crops.

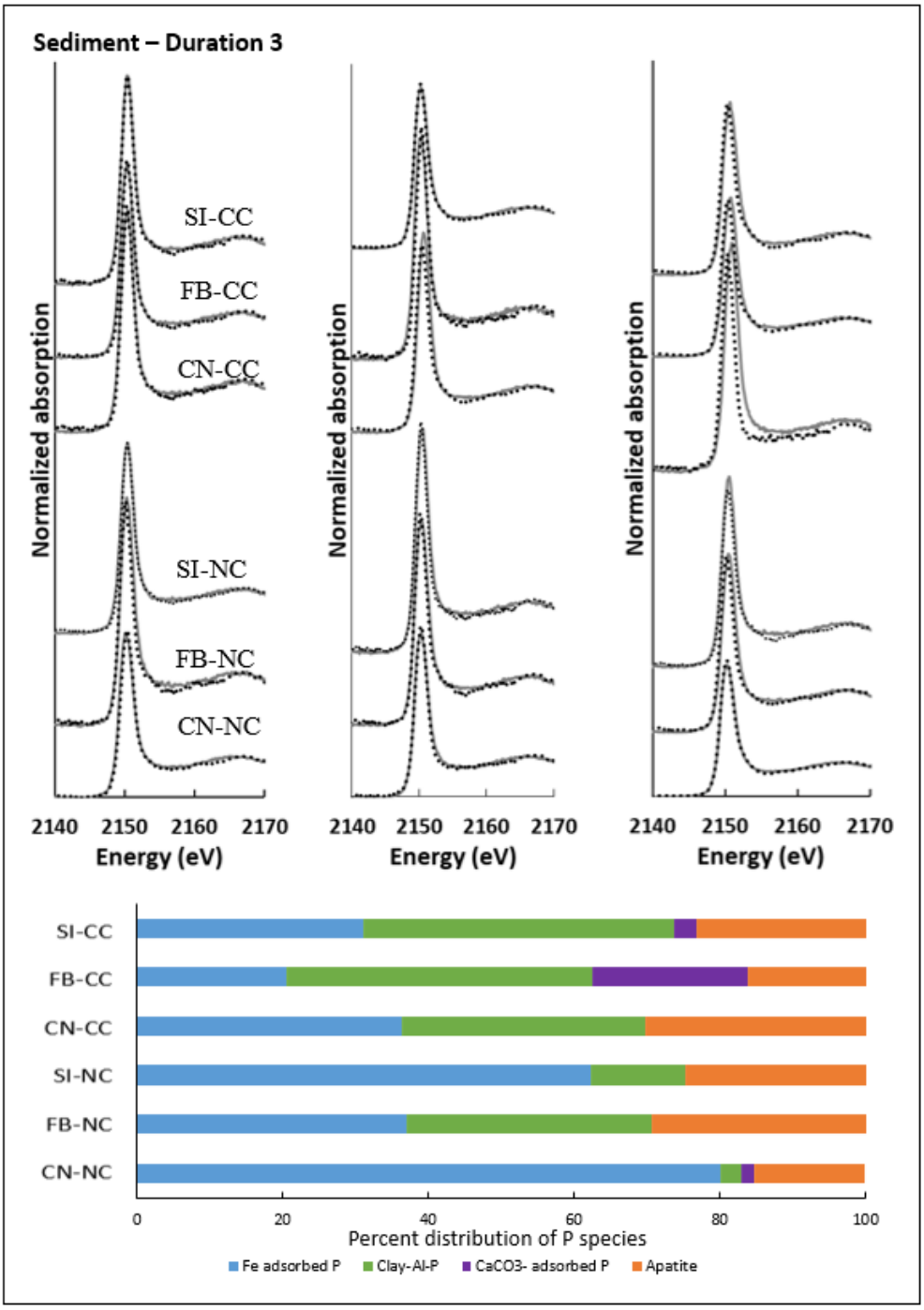


Figure 6.8. Normalized P K-edge X-ray absorption near edge structure spectra of sediment duration 3 with results of linear combination fitting as percent distribution of P species. CN-NC, control-no cover crops; FB-NC, fall broadcast-no cover crops; SI-NC, spring injection-no cover crops; CN-CC, control-with cover crops; FB-CC, fall broadcast-with cover crops; SI-CC, spring injection-with cover crops.

Summary

The findings from the sequential chemical extraction showed that P and cover crop management affected the exchangeable, organic-associated, and iron-bound P fractions in sediments and exchangeable and residual fractions in source soil. The XANES analysis showed that cover crop treatment decreased iron-associated P fraction in soil and sediments. Overall, the results suggested that the iron-associated P was more vulnerable to transformations due to cover crops. The changes in P speciation play a crucial role in the solubility of P in different P and cover crop management systems. Further research is needed on how iron chemistry changes in soil with cover crops. Particle size distribution for sediment samples will support the understanding of underlying processes in which fraction of soil is more susceptible to change in the P speciation soils and sediments.

Further research on iron speciation is needed to complement and better understand P speciation changes in these cropping systems with time. The findings from this study also highlight the importance of P management practices in protecting surface water quality even when other conservation practices, such as no-till and cover crops, are implemented. This knowledge will improve management recommendations and enhance the sustainability of cropping systems. Optimizing P fertilizer and cropping system management options helps maintain environmental sustainability.

Supporting Information

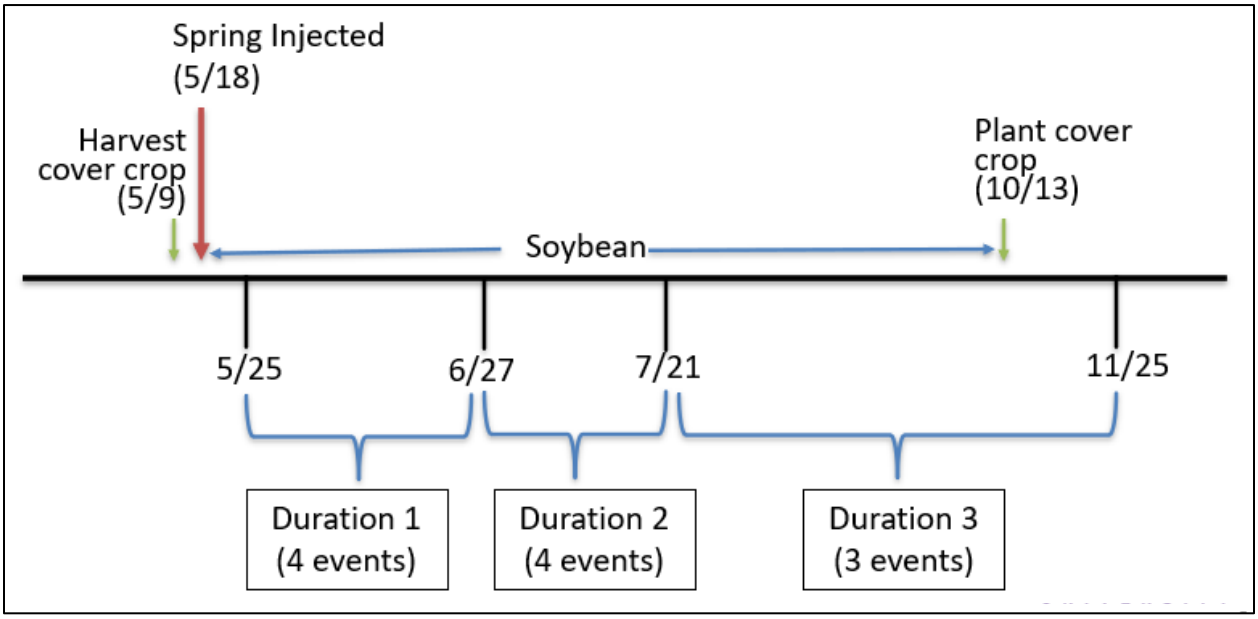


Figure 6.9. Cropping system timeline and runoff events in 2020

Table 6.2. Summary statistics for sediments (At p = 0.05 significant level according to Tukey's pairwise method).

	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Total P
Duration 1							
ptrt	<0.0001	0.0490	0.3806	0.0693	0.1823	0.7287	0.2461
cover	<0.0001	0.7910	0.0623	0.9681	0.7679	0.2197	0.9764
ptrt*cover	0.2576	0.2737	0.0135	0.6820	0.7246	0.3737	0.0515
Duration 2							
ptrt	<0.0001	0.0395	0.4079	0.0588	0.0972	0.9550	0.0999
cover	0.0049	0.6919	0.8700	0.9080	0.9654	0.9431	0.8477
ptrt*cover	0.3827	0.2167	0.4055	0.7046	0.2064	0.7640	0.1320
Duration 3							
ptrt	<0.0001	0.0440	0.4128	0.1482	0.2851	0.8435	0.1248
cover	0.0071	0.9972	0.7664	0.7531	0.7044	0.5204	0.9158
ptrt*cover	0.3642	0.5450	0.5091	0.4817	0.6493	0.4521	0.3924

Step 1: Exchangeable or loosely sorbed P

Step 2: Organic associated P

Step 3: Fe-bound P

Step 4: Authigenic carbonate fluorapatite+biogenic apatite+$CaCO_3$-bound P

Step 5: Detrital apatite plus other inorganic P

Step 6: Residual P

Table 6.3. Summary statistics for source soil (At *p* = 0.05 significant level according to Tukey's pairwise method).

	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Total P
Average of Location 1, 2 and 3							
ptrt	0.0037	0.7658	0.6340	0.8733	0.8419	<0.0001	<0.0001
cover	0.3064	0.8714	0.5577	0.2314	0.5218	0.5567	0.7058
ptrt*cover	0.5265	0.5921	0.8860	0.3230	0.8734	0.6483	0.4169

Step 1: Exchangeable or loosely sorbed P

Step 2: Organic associated P

Step 3: Fe-bound P

Step 4: Authigenic carbonate fluorapatite+biogenic apatite+$CaCO_3$-bound P

Step 5: Detrital apatite plus other inorganic P

Step 6: Residual P

References

Ajiboye, B., O.O. Akinremi, Y. Hu and A. Jurgensen. 2008. XANES speciation of phosphorus in organically amended and fertilized Vertisol and Mollisol. Soil Sci. Soc. Am. J. 72: 1256-1262.

Baldwin, D. S. 1996. The phosphorus composition of a diverse series of Australian sediments. Hydrobiologia. 335: 63–73.

Baulch, H.M., J.A. Elliott, M.R.C. Cordeiro, D.N. Flaten, D.A. Lobb, and H.F. Wilson. 2019. Soil and water management practices: opportunities to mitigate nutrient losses to surface waters in the northern Great Plains. Environ. Rev. https://doi.org/10.1139/er-2018-0101.

Blanco-Canqui, H., and S.J. Ruis. 2020. Cover crop impacts on soil physical properties: a review. Soil Sci. Soc. Am. J. 84: 527–1576.

Blanco-Canqui, H., M.M. Mikha, D.R. Presley, and M.M. Claassen. 2011. Addition of cover crops enhances no-till potential for improving soil physical properties. J Soil Water Conserv. 75(4): 1471-1482.

Bordoli, J.M. and A.P. Mallarino. 1998. Deep and shallow banding of phosphorus and potassium as alternatives to broadcast fertilizer for no-till corn. Agron. J. 90: 27-33.

Carver, R.E., N. O. Nelson, K. L. Roozeboom, G. J. Kluitenberg, P. J. Tomlinson, Q. Kang, D. S. Abel. 2022. Cover crop and phosphorus fertilizer management impacts on surface water quality from a no-till corn-soybean rotation. J. Environ. Manage. 301: 113818. https://doi.org/10.1016/j.jenvman.2021.113818.

Christianson, R., J. Fox, C. Wong, D. Caraco, A. Daniels, N. Law, and B. Stack. 2017. Literature Review and Synthesis of the Effectiveness of Cover Crops for Water Quality Management in the Upper Mississippi River Basin (White Paper). Center for Watershed Protection, Inc., Ellicott City, Maryland.

Daryanto, S., L. Wang, and P.A. Jacinthe. 2017. Meta-analysis of phosphorus loss from no-till soils. J. Environ. Qual. 46: 1028-1037.

Dodds, W.K., J.L. Eitzmann, T.J. Pilger, K.L. Pitts, A.J. Riley, J.T. Schloesser and D.J. Thornburgh. 2009. Eutrophication of U.S. freshwaters: Analysis of potential economic damages. Environ. Sci. Technol. 43: 12-19.

Dube, E., C. Chiduza, and P. Muchaonyerwa. 2014. High biomass yielding cover crops can improve soil phosphorus availability. S. Afr. J. Sci. 110(3/4): 1–4. http://dx.doi.org/10.1590/sajs.2014/20130135

Eichler-Löbermann, B., S. Köhne, B. Kowalski, and E. Schnug. 2008. Effect of catch cropping on phosphorus bioavailability in comparison to organic and inorganic fertilization. J. Plant Nutr. 31: 659-676.

Fendorf, S. E., and D.L. Sparks. 1996. X-ray absorption fine structure spectroscopy. Methods Soil Anal. Part 3. 377–416.

Hallama, M., C. Pekrun, H. Lambers, and E. Kandeler. 2019. Hidden miners – the roles of cover crops and soil microorganisms in phosphorus cycling through agroecosystems. Plant Soil. 434: 7-45.

Hesterberg, D., W.Q. Zhou, K.J. Hutchison, S. Beauchemin, and D.E. Sayers. 1999, XAFS study of adsorbed and mineral forms of phosphate. J. Synchrotron Radiat. 6: 636-638.

Hettiarachchi, G. M., M. J. McLaughlin, K. G. Scheckel, D. J. Chittleborough, M. Newville, S. Sutton, and E. Lombi. 2008. Evidence for Different Reaction Pathways for Liquid- and Granular-Micronutrients in a Calcareous Soil. Soil Sci. Soc. Am. J. 72: 98-110.

Hudnell, H. K. 2010. The state of U.S. freshwater harmful algal blooms assessments, policy and legislation. Toxicon. 55(5): 1024-34.

Johnson, S.E., and R. H. Loeppert. 2006. Role of organic acids in phosphate mobilization from iron oxide. Soil Sci. Soc. Am. J. 70: 222–234.

Kar, G., L.S. Hundal, J.J. Schoenau, and D. Peak. 2011. Direct chemical speciation of P in sequential chemical extraction residues using P K edge X-ray absorption near edge structure spectroscopy. Soil Sci. 176: 589−595.

Khatiwada, R., G.M. Hettiarachchi, D. Mengel, and M. Fei. 2012. Speciation of Phosphorus in a Fertilized Reduced Till Soil System: In-Field Treatment Incubation Study. Soil Sci. Soc. Am. J. 76: 2006-2018.

Kizewski, F., Y.T. Liu, A. Morris, and D. Hesterberg. 2011. Spectroscopic approaches for phosphorus speciation in soils and other environmental systems. J. Environ. Qual. 40,: 751−766.

Kruse, J., and P. Leinweber. 2008. Phosphorus in sequentially extracted fen peat soils: A K-edge X-ray absorption near-edge structure (XANES) spectroscopy study. J. Plant Nutr. and Soil Sci. 171:613-620.

Li, W., S. R. Joshi, S. Hou, D. J. Burdige, D. L. Sparks, and D. P. Jaisi. 2015. Characterizing Phosphorus Speciation of Chesapeake Bay Sediments Using Chemical Extraction, 31P NMR, and X-ray Absorption Fine Structure Spectroscopy. Environ. Sci. Technol. 49(1): 203-211.

Li, Y., T.P. Abegunrin, H. Guo., Z. Huang, K.S. Are, H. Wang, M. Gu., and L. Wei. 2020. Variation in dissolved nutrient exports by surface runoff from sugarcane watershed is controlled by fertilizer application and ground cover. Ag. Eco. Environ. 303: 107121. https://doi.org/10.1016/j.agee.2020.107121

Liu, J., J. Yang, B.J. Cade-Menun, X. Liang, Y. Hu, C.W. Liu, Y. Zhao, L. Li, and J. Shi. 2013. Complementary phosphorus speciation in agricultural soils by sequential fractionation, solution 31P nuclear magnetic resonance, and phosphorus K-edge X-ray absorption near edge structure spectroscopy. J. Environ. Qual. 42: 1763−1770.

Lombi E., G.M. Hettiarachchi, and K.G. Scheckel. 2011. Advanced in situ spectroscopic techniques and their applications in environmental biogeochemistry: Introduction to the special section. J. Environ. Qual. 40: 659-666.

Lombi, E., K.G. Scheckel, R.D. Armstrong, S. Forrester, J.N. Cutler and D. Paterson. 2006. Speciation and distribution of phosphorus in a fertilized soil: A synchrotron-based investigation. Soil Sci. Soc. Am. J. 70: 2038–2048.

Loss, A., A. Brass, B.S. Oliveira, L.P. Koucher, R.A. Oliveiria, C. Kurtz, P.E. Lovato, P. Curmi, G. Brunetto, and J.J. Comim. 2015. Total organic carbon and soil aggregation under a no-

tillage agroecological system and conventional tillage system for onion. Rev. Bras. Cienc Solo. 39: 1212–1224.

Machesky, M.L., T.R. Holm, and J.A. Slowikowski. 2010. Phosphorus Speciation in Stream Bed Sediments from an Agricultural Watershed: Solid-Phase Associations and Sorption Behavior. Aquat Geochem. 16: 639–662. https://doi-org.er.lib.k-state.edu/10.1007/s10498-010-9103-2.

Macrae, M., H. Jarvie, R. Brouwer, G. Gunn, K. Reid, P. Joose, K. King, P. Kleinman, D. Smith, M. Williams, and M. Zwonitzer. 2021. One size does not fit all: toward regional conservation practice guidance to reduce phosphorus risk loss in the Lake Erie watershed. J. Environ. Qual. 50: 529–546.

Milani, N., G.M. Hettiarachchi, D.G. Beak, M. J. McLaughlin, J. K. Kirby, and S. P. Stacey. 2015. Fate of zinc oxide nanoparticles coated onto macronutrient fertilizers in an alkaline calcareous soil. PLoS One.10(5): e0126275.

Moody, P. W. 2011. Environmental risk indicators for soil phosphorus status. Soil Res. 49: 247-252.

Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27: 31-36.

NRCS. 2015. Soil health literature summary – Effects of conservation practices on soil properties in areas of crop land. Natural Resources Conservation Service, National Soil Survey Center. United States Department of Agriculture.

Peak, D., J.T. Sims, and D.L. Sparks. 2002. Solid-state speciation of natural and alum-amended poultry litter using XANES spectroscopy. Environ. Sci. Technol. 36: 4253−4261.

Pote, D.H., T.C. Daniel, D.J. Nichols, A.N. Sharpley, P.A. Moore, Jr., D.M. Miller, and D.R. Edwards. 1999. Relationship between phosphorus levels in three Ultisols and phosphorus concentration in runoff. J. Environ. Qual. 28: 170-175.

Ravel B., and M. Newville. 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12: 537–541.

Ruffatti, M.D., R.T. Roth, C.G. Lacey, and S.D. Armstrong. 2019. Impacts of nitrogen application timing and cover crop inclusion on subsurface drainage water quality. Agric. Water Manag. 211: 84–88.

Ruttenberg, K. C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Geochim. Cosmochim. Acta. 37: 1460−1482.

SAS Institute. 2011. The SAS system for Windows version 9.1.3. SAS Institute, Cary, NC.

Sharpley, A., and H. Tunney. 2000. Phosphorus research strategies to meet agricultural and environmental challenges of the 21st Century. J. Environ. Qual. 29: 176-181.

Sharpley, A.N., S.J. Smith, O.R. Jones, W.A. Berg., and G.A. Coleman. 1992. The transport of bioavailable phosphorus in agricultural runoff. J. Environ. Qual. 21: 30-35.

Sims, J. T., A.C. Edwards, O.F. Schoumans, and R.R. Simard. 2000. Integrating soil phosphorus testing into environmentally based agriculture management practices. J. Environ. Qual. 29: 60-71.

Smith, D. R., S.J. Francesconi, S.J. Livingston, and C. Huang. 2015. Phosphorus losses from monitored fields with conservation practices in the Lake Erie Basin, USA. Ambio. 44(2): S319-S331.

Smith, D.R., P.A. Moore Jr., C.V. Maxwell, B.E. Haggard, and T.C. Daniel. 2004a. Reducing phosphorus runoff from swine manure with dietary phytase and aluminum chloride. J. Environ. Qual. 33: 1048-1054.

Smith, D.R., P.A. Moore Jr., D.M. Miles, B.E. Haggard, and T.C. Daniel. 2004b. Decreasing phosphorus runoff losses from land-applied poultry litter with dietary modifications and alum addition. J. Environ. Qual. 33: 2210-2216.

Smith, D.R., P.R. Owens, A.B. Leytem, and E.A. Warnemuende. 2007. Nutrient loss from manure and fertilizer applications as impacted by time to first runoff event. Environ. Pollut. 147: 131-137.

Smith, D.R., R.D. Harmel, M. Williams, R. Haney, and K.W. King. 2016. Managing acute phosphorus loss with fertilizer source and placement: Proof of concept. Agric. Environ. Lett. 1:150015

Starr, L.M. 2021. Linkages between cover crops, phosphorus fertilizer management, soil health, and phosphorus bioavailability in replicated research watersheds [Doctoral Dissertation, Kansas State University] K-State Research Exchange.

TerAvest, D., L. Carpenter-Boggs, C. Thierfelder, and J.P. Reganold. 2015. Crop production and soil water management in conservation agriculture, no-till, and conventional tillage systems in Malawi. Agriculture, Ecosystems and Environment. 212: 285–296.

Torbert H.A., K.N. Potter, D.W. Hoffman, T.J. Gerik, and C.W. Richardson. 1999. Surface residue and soil moisture affect fertilizer loss in simulated runoff on a heavy clay soil. Agron. J. 4: 606–612.

Violante, A., and L. Gianfreda. 1993. Competitive adsorption between phosphate and oxalate on an aluminum hydroxide montmorillonite complex. Soil Sci. Soc. Am. J. 57: 1235-1241.

Wang, Y., Q. Huang, H. Gao, R. Zhang, L. Yang., Y. Guo, H. Li, M.K. Awasthi, and G. Li. 2021. Long-term cover crops improved soil phosphorus availability in a rain-fed apple orchard. Chemosphere. 275: 130093. https://doi.org/10.1016/j.chemosphere.2021.130093

Weeks, J. J., and G. M. Hettiarachchi. 2020. Source and Formulation Matter: New Insights into Phosphorus Fertilizer Fate and Transport in Mildly Calcareous Soils. Soil Sci. J. Am. 84: 731-746. https://doi.org/10.1002/saj2.20054

Werner, F., and J. Prietzel. 2015. Standard protocol and quality assessment of soil phosphorus speciation by P K-edge XANES spectroscopy. Environ. Sci. Technol. 49: 10521-10528.

Chapter 7 - Overall Summary and Implications

The increasing demand for P sources and concerns about surface water quality raise the need to explore safe and efficient secondary P fertilizer sources. The RNPs recovered from wastewater may contain high concentrations of plant-available nutrients, and thus, they can be effective alternative fertilizers. Currently, minimal data is available on these RNPs and their potential behavior in soils to decide their ability to act as secondary P sources. Therefore, to address that, the first three studies were designed to characterize and compare the RNPs recovered from different wastewater sources as municipal, synthetic swine, and real swine wastewater using an innovative AnMBR technology and to investigate the dissolution, transformations, and potential bioavailability of P in the RNPs with conventional P fertilizers in selected soils using short-term laboratory incubation studies combined with wet chemical and synchrotron-based X-ray techniques.

The RNP recovered from municipal wastewater was rich in Fe-P as Fe was used in the P recovery process, but the total P content was only ~2.6%. The P diffusion and PRP results demonstrate that P in RNP was not mobile or resin extractable compared to conventional fertilizers, MAP, and TSP in mildly calcareous soil. The results suggested that the RNP did not perform effectively as a fertilizer, but it did demonstrate the capacity to absorb P and acted as a P sink. Therefore, the findings of this work revealed that incorporating Fe-based RNP into the best management practices for biosolids or manure field applications can be beneficial. It can significantly reduce solubility of fertilizer P and effectively tackle the issue of excessive dissolved reactive P commonly found in runoff from land-applied nutrient enriched organic P sources. This could be a worthwhile approach that can help mitigate the potential environmental hazards associated with P runoff.

The RNPs recovered from synthetic and real swine wastewater were rich in Ca-P, as Ca was used in the P recovery process. The total P contents were 11.5% and 11.1% for synthetic and real swine wastewater RNPs, respectively. The synthetic swine wastewater-derived RNP acted as a P source for all three, calcareous, neutral, and acid, soils tested. The real swine wastewater-derived RNP also acted as a P source for the select neutral soil (it was the only soil tested with this RNP). The P diffusion and resin extractability (potential plant availability) results demonstrated that these RNPs had lower solubility and extractability than conventional fertilizers (MAP and TSP) in the tested soils. The direct speciation of P using XANES spectroscopy further revealed differences in P speciation among control soil and various P-added treatments. The RNPs showed more insoluble precipitated species like hydroxyapatite, which explains the reduced solubility and extractability of these RNPs in the tested soils. Both RNPs buffered the soil pH around the product's original pH due to the residual alkalinity of the product.

The P investigations of RNPs have yielded crucial insights into P dissolution, transformations, and reaction pathways affecting the P fertilizer use efficiency in different agricultural systems. However, due to the diversity of RNPs in terms of physical and chemical properties, variations in recovery methods, and residual alkalinity levels, the estimated fertilizer value of the recovered materials may vary. Thus, studying these products from different wastewater sources and soil types is essential. To gain a more thorough understanding of P dissolution, transformations, and P species and to optimize P recovery, detailed laboratory experiments of RNPs are necessary. The feedback from these experiments can help improve and enhance P recovery efficiency. After optimization, greenhouse and field-scale studies can be conducted to test the recovered products further. Optimizing Ca-P recovery has the potential to create practical and versatile secondary P sources that are not N-based, such as struvite, which

can benefit and crucial to sustainable and circular agricultural production. Therefore, it is essential to explore RNPs more to understand their full potential as a sustainable and efficient secondary P fertilizer source.

Phosphorus loss from agricultural fields contributes to reduced water quality and eutrophication. Conservation management has been shown to decrease erosion and improve soil health. However, more research needs to be conducted on how P and cover crop management practices influence P speciation in agricultural soils and runoff sediments to make informed recommendations on best management practices. The current study was designed to characterize and evaluate the effects of a five-year-long P fertilizer (placement and source) and cover crop management (no cover crop and with cover crop) on P speciation in surface runoff sediments from natural precipitation events and source soils, collected from Kansas Agricultural Watershed (KAW) field laboratory Manhattan, Kansas under no-till corn (*Zea mays* L.) and soybean (*Glycine max* L.) rotation. The findings from the sequential chemical extraction showed that P and cover crop management affected the exchangeable, organic-associated, and iron-bound P fractions in sediments and exchangeable and residual fractions in source soil. The XANES analysis showed that cover crop treatment decreased iron-associated P fraction in soil and sediments. Depletion of Fe-associated P in soil and sediment from cover crop systems suggested that Fe-associated P was more vulnerable to transformations due to cover crops. Based on these results, we suspect that reduced iron-associated P likely resulted in more labile P. Further studies are needed to understand changes in iron chemistry with different cover crops.

This study emphasizes the importance of implementing specific conservation strategies, keeping in mind that the significant impact that changes in agricultural management practices can have on the soil, sediments, and the environment. Since protecting and promoting water

quality is a complex challenge that requires a systemic approach, it is crucial to develop multifaceted solutions. Understanding the P speciation can provide valuable insights leading to more informed management recommendations and enhanced cropping system sustainability. Optimizing P fertilizer and cropping system management options is crucial to maintaining environmental sustainability.