University of São Paulo
Luiz de Queiroz College of Agriculture

Phosphorus dynamics in soils amended with alternative sources of phosphate fertilizers

Rodrigo Nogueira de Sousa

Thesis presented to obtain the degree of Doctor in Science. Area: Soil and Plant Nutrition

Piracicaba
2023

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1. Fonte alternativa de P 2. Extratores 3. Eficiência agronômica 4. Bactérias solubilizadoras de P 5. Curvas de breakthrough I. Título

To my grandparents, especially my grandmother Elça Nogueira and grandfather João Cordeiro, who cultivated the land and lived from it until the last days of their lives, brilliantly passing on all their wisdom and love to my parents. To my father, Vanildo Cordeiro, who inherited his father's love for agriculture and sowed it in my heart before he left this earth. To my mother, Eleny Nogueira, who cultivates the land and from it earns her livelihood...

*I **dedicate** every minute spent on this thesis.*

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To God for all that I am. MY ETERNAL AND DEEPEST GRATITUDE!!!!!

BIOGRAPHY

RODRIGO NOGUEIRA DE SOUSA, son of Eleny Aparecida Nogueira Sousa and Vanildo Cordeiro de Sousa, was born on April 19, 1990, in Santo Antônio do Leste, Mato Grosso, Brazil. In 2010, he enrolled in the Agronomy program at the Federal University of Viçosa, completing his studies in July 2016.

From March 2014 to July 2015, he was a scholarship recipient of the Science without Borders/CAPES program, participating in the "sandwich undergraduate" modality at North Carolina Agricultural and Technical State University (NCA&T). Between May and July 2015, he completed an internship under the "Academic Training" modality at North Carolina State University (NC State University).

In August 2016, he entered the graduate program in Soil Science and Plant Nutrition at the Master's level, specializing in soil fertility, at the Federal University of Viçosa.

In August 2018, he entered the doctoral (Ph.D.) level program in Soil Science and Plant Nutrition, in the Graduate Program in Soils and Plant Nutrition, at the Luiz de Queiroz College of Agriculture – ESALQ – University of São Paulo (USP).

“Change places, but don't forget your roots.
Think differently, but don't lose your principles.
Change is necessary, but ensure that your "new self"
is a source of pride for your "former self."
(Talita Galhardo)

Estude, estude, estude sempre...
(Vanildo Cordeiro – meu pai)

"É preciso amor pra poder pulsar
É preciso paz pra poder sorrir
É preciso a chuva para florir...”

Penso que cumprir a vida
Seja simplesmente
Compreender a marcha
E ir tocando em frente...

Cada um de nós compõe a sua história
Cada ser em si
Carrega o dom de ser capaz
E ser feliz”
(Almir Sater)

O saber a gente aprende com os mestres e os livros.
A sabedoria se aprende é com a vida e com os humildes.
(Cora Coralina)

CONTENTS

RESUMO

Dinâmica do fósforo em solos tratados com fontes alternativas de adubos fosfatados

A necessidade de adubação fosfatada em solos tropicais é ressaltada pela intensa produção agrícola do Brasil e sua alta dependência de importação de fertilizantes. Com mais de 70% dos fertilizantes agrícolas, incluindo fosfatos, sendo importados, torna-se urgente a busca por fontes alternativas de fertilizantes. Essas alternativas são cruciais para melhorar a utilização de fósforo na agricultura, especialmente em solos tropicais onde a disponibilidade de fosfato é frequentemente limitada, abordando preocupações tanto econômicas quanto de sustentabilidade ambiental. A dinâmica do fósforo (P) tem fascinado pesquisadores globalmente desde sua identificação como elemento crucial para a vida. Esse elemento apresenta alta reatividade no solo e é um dos mais limitantes para a produção agrícola em solos de regiões tropicais úmidos. Esta tese integra abordagens multidisciplinares para compreender aspectos químicos, físicos e biológicos do solo em resposta aos fertilizantes fosfatados. A tese tem início no capítulo 2 com um estudo em que foi investigada a precisão extratores de teores disponíveis de P (resina, Mehlich-1 e Mehlich-3) em solos tropicais cultivados com milho (*Zea mays*) e fertilizados com fonte mineral e alternativas de P. A resina teve a melhor correlação com a absorção de P pelas plantas, o que demonstrou sua eficácia em solos altamente intemperizados, enquanto Mehlich-1 e Mehlich-3 tenderam a superestimar os valores de P. Os desempenhos dos fertilizantes estruvita (Est), organomineral (OM) e termofosfato (ThermoP) e superfosfato triplo (TSP) em cultivos de milho foram avaliados no cap. 3 por meio de índices de eficiências agronômicas. Est e OM superaram o TSP no solo franco-arenoso, com quase o dobro da eficiência em comparação com o solo argiloso. A liberação lenta de nutrientes por essas fontes alternativas resultou em melhor aproveitamento de P pelas plantas. Os efeitos dos fertilizantes mineral e alternativos na microbiota do solo e na biomassa de milho foram explorados no cap. 4, sendo que Est e OM não só melhoraram o status de P no solo, mas também enriqueceram as comunidades microbianas e levaram ao aumento da biomassa de parte aérea do milho. O OM proporcionou aumento nas frações de P e na diversidade microbiana, enquanto a Est promoveu a proliferação de bactérias solubilizadoras de P, incluindo gêneros benéficos. Por fim, o deslocamento miscível de P em solos tropicais foi avaliado no cap. 5 com avaliações do pH do solo, textura e fontes de P. Por meio de um experimento com colunas, simulou-se o movimento de P em perfis de solo sob diferentes condições de pH e constatou-se que ajustes no pH do solo afetaram a dinâmica do P, o que enfatiza a importância de estratégias de fertilização balanceadas para otimizar a disponibilidade de P e minimizar o risco de lixiviação, especialmente em solos arenosos. Esses capítulos, em conjunto, oferecem uma visão abrangente sobre a eficácia de fontes alternativas de fertilizantes de P em solos tropicais úmidos e realçam seu impacto positivo na disponibilidade de nutrientes, meio ambiente, saúde do solo e produtividade agrícola.

Palavras-chave: Fonte alternativa de P, Extratores, Eficiência agronômica, Bactérias solubilizadoras de P, Curvas de *breakthrough*

ABSTRACT

Phosphorus dynamics in soils amended with alternative sources of phosphate fertilizers

The need for phosphate fertilization in tropical soils is underscored by Brazil's significant agricultural production and high dependence on fertilizer imports. With over 70% of agricultural fertilizers, including phosphates, imported, there is an urgent need to explore alternative fertilizer sources. These alternatives are crucial to improve phosphorus use in agriculture, especially in tropical soils where phosphate availability is often limited, addressing both economic and environmental sustainability concerns. The dynamics of phosphorus (P) have captivated researchers worldwide since its recognition as an essential element for life. This element has high reactivity in soils and is often a limiting factor for agricultural production in humid tropical regions. Overall, this thesis integrates multidisciplinary approaches to understand the chemical, physical, and biological aspects of soil in response to alternative phosphate fertilizers. The thesis begins in Chapter 2 with a study of the accuracy of extractors for available P contents (resin, Mehlich-1, and Mehlich-3) in tropical soils grown with maize (*Zea mays*) and fertilized with mineral and alternative P sources. The resin method had the best correlation with plant P uptake, demonstrating its effectiveness in highly weathered soils, while Mehlich-1 and Mehlich-3 methods tended to overestimate P values. In chapter 3, the performances of struvite (Est), organomineral (OM), thermophosphate (ThermoP), and triple superphosphate (TSP) fertilizers in maize yield were evaluated by means of agronomic efficiency indices. Est and OM outperformed TSP in the sandy-loamy soil, with almost twice the efficiency compared to a clayey soil. The slow release of nutrients from these alternative sources resulted in better P utilization by plants. The effects of mineral and alternative P fertilizers on soil microbiota and maize biomass were explored in chapter 4. Est and OM fertilizers not only improved soil P status but also enriched microbial communities and increased maize biomass. OM fertilizer enhanced P fractions and microbial diversity, while Est promoted the proliferation of P-solubilizing bacteria, including beneficial genera. Finally, the miscible displacement of P in tropical soils, considering soil pH, texture, and P sources were evaluated in chapter 5. A column experiment was used to simulate the movement of P in soil profiles under varying pH conditions. Adjustments in soil pH affected P dynamics, emphasizing the importance of balanced fertilization strategies to optimize P availability and minimize leaching risk, especially in sandy soils. Taken together, these chapters provide a comprehensive view of the efficacy of alternative P fertilizer sources in humid tropical soils and highlight their positive impact on nutrient availability, environmental, soil health, and agricultural productivity.

Keywords: Alternative P source, Extractors, Agronomic efficiency, P-solubilizing bacteria, Breakthrough curves

1. GENERAL INTRODUCTION

Fertilizer consumption in Brazil is among the five highest in the world. About 41 million tons were consumed by the country in 2022 (ANDA, 2022). Brazil ranks third in terms of phosphate fertilizer consumption, behind India and China, which ranks first (Vegro, 2023). This large consumption is justified by the country's global superpower in agricultural production. Although Brazil has achieved high levels of agricultural production, the same is not true for fertilizer production. The National Association for the Diffusion of Fertilizers (ANDA) reports that more than 70% of Brazil's agricultural fertilizers are imported, with the highest dependence on potassium chloride (95%), nitrogen (80%) and phosphate (60%).

Influenced by global market trends and currency fluctuations, fertilizer prices in Brazil vary significantly throughout the year, requiring strategic planning by farmers (Farias et al., 2020). This reliance on imported fertilizers exposes Brazil to international supply volatility, which has a direct impact on agricultural production and market stability. Fertilizers represented approximately 40% of agricultural production costs in 2022 (CONAB, 2022).

Due to the high external dependence and the non-renewable nature of phosphate rock, there is an urgent need for research into alternative sources to improve phosphorus (P) use in agriculture. Given this scenario of high external dependency, combined with the fact that phosphate rock is non-renewable, research is needed into new alternative sources aimed at increasing the use of phosphorus in agriculture.

The production and agronomic use of economically viable alternative sources, such as organomineral (OM) fertilizers, which combine mineral and organic components, present interesting areas for study. OM fertilizers are increasingly produced in Brazil, leading the Ministry of Agriculture, Livestock and Supply (MAPA) to issue a new normative instruction in July 2020 to regulate their production (Brasil, 2020).

Alternative phosphate fertilizers such as OM not only provide nutrients but also serve as sources of organic matter, and this leads to numerous benefits for improving the chemical and biological environment of the soil (Borges et al., 2019). The combination of mineral and organic matter leads to a greater release of P into solution in soils with high adsorption capacity due to reduced P fixation and more efficient use of P by plants, thus increasing productivity (Eghball et al., 1996; Dotaniya and Datta, 2014; Withers et al., 2018). In addition, enhanced P cycling is observed in agricultural systems where organic sources are applied because of the increased activity of microorganisms immobilizing inorganic P and mineralization of organic P (Richardson and Simpson, 2011; Requejo and Eichler-Löbermann, 2014).

One of the positive factors of fertilizing with organic sources is the maintenance and increase of the organic matter content in the soil, which provides nutrients, increases water retention, and promotes improvements in the physical properties of the soil (Mohammadi et al., 2011; Pekcan et al., 2021). Borges et al. (2019), Frazão et al. (2019) and Crusciol et al. (2020) have shown that plants use P from OM more effectively than from mineral sources. However, how surface chemical phenomena such as sorption and desorption occur between P from these alternative sources and soil colloids is still uncertain.

Another alternative source of P widely used in agriculture in some countries, such as Germany and France, is struvite (Est) - ($MgNH_4PO_4$-$6H_2O$). Est is obtained from the recovery of P from sewage sludge wastewater (Muryanto, 2017) and has a high potential for agricultural use (Muys et al., 2021). The precipitation of this mineral occurs in watery systems with elevated concentrations of phosphate and ammonia (Tansel et al., 2018). Moreover, its formation is influenced by factors such as pH, temperature, and the concentration of ions that make up the struvite crystals.

Est has shown notable agronomic efficiency due to its unique nutrient-release properties. For instance, in a comparative study on maize (*Zea mays*) cultivation, struvite had a slower, more controlled release of P than traditional fertilizers (Muys et al., 2021). This gradual nutrient release not only ensures a consistent supply of P over a longer period but also minimizes the risk of nutrient leaching, thereby improving the overall nutrient uptake efficiency of the crop (Kataki et al., 2016). Such Est properties are particularly beneficial in soils prone to rapid nutrient depletion and reinforce its potential to improve crop yields while promoting sustainable farming practices (Vejan et al., 2021).

Another method of recovering P from sewage sludge is its incineration at temperatures between 850-900°C in a thermochemical process that concentrates nutrients and eliminates pollutants. A P-enriched ash is then produced and can be used in agriculture. Ashdec® (Ash) is a thermophosphate produced from phosphorus-rich ash left over from sewage sludge, animal products, agricultural waste such as chicken litter, and other nutrient-rich organic residues (Adam et al., 2009). In the thermochemical process, alkaline compounds are decomposed at high temperatures and react with phosphates to form bioavailable P compounds. Thus, a concentrated P fertilizer is produced after appropriate ash treatment (Ohtake and Tsuneda, 2019). Sewage sludge ash has a higher relative effectiveness in acidic soils than in alkaline soils (Nanzer et al., 2014).

The use of alternative P sources has undeniable potential, especially in humid tropical soils where challenges such as high weathering and acidity often impede nutrient availability.

A critical area of research is the interaction of these alternative fertilizers with different soil types, including their effects on soil fauna and the dynamics of P availability. These aspects require a comprehensive understanding to optimize the efficient use of P by plants from these fertilizers. In addition to the biological effects, the chemical interactions between these fertilizers and soil colloids are crucial. This includes evaluating labile or non-labile P forms. Such knowledge is essential to improve the efficacy of fertilizers in different soil conditions. In addition, it is extremely important to study the miscible displacement of phosphate ions from these sources to recommend ideal doses for crop production that do not cause environmental contamination.

This thesis integrates multi-disciplinary approaches to understand the chemical, physical, and biological aspects of soil in response to phosphate fertilizer. The objectives in this study were: (i) to evaluate which of the extractors provided the most accurate and reliable measurements of available P on two soils with contrasting textures and whether the type of P fertilizer affected the extraction efficiency of these extractors, (ii) to compare the effectiveness of conventional phosphorus fertilizer (triple superphosphate, TSP) with alternative sources (struvite, organomineral, and thermophosphate) in improving maize yield, (iii) to elucidate the impacts of mineral and organic P sources on soil microbial communities and their functional profiles within the rhizosphere of maize cultivated in two contrasting soils, and (iv) to evaluate how soil pH, texture, and P sources influence the miscible displacement of phosphatic ion in sandy-loamy and clayey soils.

References

Adam, C., Peplinski, B., Michaelis, M., Kley, G., & Simon, F. G. (2009). Thermochemical treatment of sewage sludge ashes for phosphorus recovery. Waste Management, 29(3), 1122–1128. https://doi.org/10.1016/j.wasman.2008.09.011

ANDA - Associação Nacional Para Difusão de Adubos. (2022). Anuário estatístico do setor de Fertilizantes 2021. São Paulo: ANDA, 176 p.

Borges, B. M. M. N., Abdala, D. B., Souza, M. F. D., Viglio, L. M., Coelho, M. J. A., Pavinato, P. S., & Franco, H. C. J. (2019). Organomineral phosphate fertilizer from sugarcane byproduct and its effects on soil phosphorus availability and sugarcane yield. Geoderma, 339, 20–30. https://doi.org/10.1016/j.geoderma.2018.12.036

Brasil. (2020). Instrução Normativa n° 61, de 08 de julho de 2020. Estabelece as regras sobre definições, exigências, especificações, garantias, tolerâncias, registro, embalagem e rotulagem dos fertilizantes orgânicos e dos biofertilizantes, destinados à agricultura.

CONAB – Companhia nacional de abastecimento. 2022. 6º levantamento da safra de grãos 21/22. Available in <https://www.canalrural.com.br/programas/mercado-e-cia/peso-de-fertilizantes-no-custo-de-producao/>. Accessed December 16, 2023.

Crusciol, C. A. C., Campos, M. D., Martello, J. M., Alves, C. J., Nascimento, C. A. C., Pereira, J. C. D. R., & Cantarella, H. (2020). Organomineral Fertilizer as Source of P and K for Sugarcane. Scientific Reports, 10(1). https://doi.org/10.1038/s41598-020-62315-1

Dotaniya, M. L., & Datta, S. C. (2013). Impact of Bagasse and Press Mud on Availability and Fixation Capacity of Phosphorus in an Inceptisol of North India. Sugar Tech, 16(1), 109–112. https://doi.org/10.1007/s12355-013-0264-3

Eghball, B., Binford, G. D., & Baltensperger, D. D. (1996). Phosphorus Movement and Adsorption in a Soil Receiving Long-Term Manure and Fertilizer Application. Journal of Environmental Quality, 25(6), 1339–1343. https://doi.org/10.2134/jeq1996.00472425002500060024x

Farias, P. I. V., Freire, E., Cunha, A. L. C., Grumbach, R. J. D. S., & Antunes, A. M. S. (2020). The Fertilizer Industry in Brazil and the Assurance of Inputs for Biofuels Production: Prospective Scenarios after COVID-19. Sustainability. https://doi.org/10.3390/su12218889

Frazão, J. J., Benites, V. D. M., Ribeiro, J. V. S., Pierobon, V. M., & Lavres, J. (2019). Agronomic effectiveness of a granular poultry litter-derived organomineral phosphate fertilizer in tropical soils: Soil phosphorus fractionation and plant responses. Geoderma, 337, 582–593. https://doi.org/10.1016/j.geoderma.2018.10.003

Kataki, S., West, H., Clarke, M., & Baruah, D. (2016). Phosphorus recovery as struvite: Recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential. Resources, Conservation and Recycling, 107, 142–156. https://doi.org/10.1016/j.resconrec.2015.12.009

Mohammadi, K., Heidari, G., Khalesro, S., & Sohrabi, Y. (2011). Soil management, microorganisms and organic matter interactions: A review. African Journal of Biotechnology, 10(86), 19840.

Muys, M., Phukan, R., Brader, G., Samad, A., Moretti, M., Haiden, B., Pluchon, S., Roest, K., Vlaeminck, S. E., & Spiller, M. (2021). A systematic comparison of commercially produced struvite: Quantities, qualities and soil-maize phosphorus availability. Science of the Total Environment, 756, 143726. https://doi.org/10.1016/j.scitotenv.2020.143726

Nanzer, S., Oberson, A., Berger, L., Berset, E., Hermann, L., & Frossard, E. (2014). The plant availability of phosphorus from thermo-chemically treated sewage sludge ashes as studied by 33P labeling techniques. Plant and Soil, 377(1–2), 439–456. https://doi.org/10.1007/s11104-013-1968-6

Ohtake, H., & Tsuneda, S. (2019). Phosphorus Recovery and Recycling. 1st ed. Singapore: Springer Singapore. 253 p.

Pekcan, T., & Turan, H. S. (2021). Importance of organomineral fertilizers in agriculture. Agricultural researches resource book. Turkey: Iksad Publishing House, pp. 243-274.

Requejo, M. I., & Eichler-Löbermann, B. (2014,). Organic and inorganic phosphorus forms in soil as affected by long-term application of organic amendments. Nutrient Cycling in Agroecosystems, 100(2), 245–255. https://doi.org/10.1007/s10705-014-9642-9

Richardson, A. E., & Simpson, R. J. (2011). Soil Microorganisms Mediating Phosphorus Availability Update on Microbial Phosphorus. Plant Physiology, 156(3), 989–996. https://doi.org/10.1104/pp.111.175448

Tansel, B., Lunn, G., & Monje, O. (2018). Struvite formation and decomposition characteristics for ammonia and phosphorus recovery: A review of magnesium-ammonia-phosphate interactions. Chemosphere, 194, 504–514. https://doi.org/10.1016/j.chemosphere.2017.12.004

Vegro, C. L. R, Angelo, J. A. (2023). Diversificação nas Origens de Fertilizantes Importados Suplanta a Escassez Causada pelo Conflito Russo-Ucraniano. Análises e Indicadores do Agronegócio, São Paulo, Brazil, v. 18, n. 4, p. 1-8. Available in: <http://www.iea.agricultura.sp.gov.br/out/TerTexto.php?codTexto=16131>. Accessed December 16, 2023.

Vejan, P., Khadiran, T., Abdullah, R., & Ahmad, N. (2021). Controlled release fertilizer: A review on developments, applications and potential in agriculture. Journal of Controlled Release, 339, 321–334. https://doi.org/10.1016/j.jconrel.2021.10.003

Withers, P. J. A., Rodrigues, M., Soltangheisi, A., de Carvalho, T. S., Guilherme, L. R. G., Benites, V. D. M., Gatiboni, L. C., Sousa, D. M. G., Nunes, R. D. S., Rosolem, C. A., Andreote, F. D., Oliveira, A. D., Coutinho, E. L. M., & Pavinato, P. S. (2018). Transitions to sustainable management of phosphorus in Brazilian agriculture. Scientific Reports, 8(1). https://doi.org/10.1038/s41598-018-20887-z