

# Struvite potential as a slow-release fertilizer for phosphorus sustainable management in Brazilian agriculture

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**ABSTRACT:** Phosphorus in agriculture is an essential, limited, and strategic resource, and its sustainable management is a global challenge. Phosphorus (P) recovery as struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) from manures and municipal and agro-industrial wastewaters has been considered one of the most sustainable technologies, based on the circular economy, to face challenges regarding P reserves and its use for conventional fertilizer production. Struvite is a slow-release P-fertilizer (5 % N, 12 % P, 10 % Mg), which could significantly reduce the Brazilian dependency on fertilizer imports. We found a large number of recent studies that show its predominant application for temperate and Mediterranean regions. However, its potential as a fertilizer and better use for subtropical and tropical regions, such as Brazilian agriculture, is still unknown. We highlight that: (i) crop responses reported were quite variable with few field studies carried out; (ii) the crop yield expected may be on average 10 % below those in soluble P sources; (iii) a potentially high residual effect should be effectively measured; (iv) promising use of struvite mixed with soluble P-fertilizers to produce high yields; (v) higher efficiency than manure, composts or phosphate powder rocks. In fact, there is a lack of studies carried out on subtropical and tropical soils and climates; none were found in Brazil. Therefore, the lack of studies on Brazilian soils is a barrier to a precise evaluation of struvite as a fertilizer for Brazil's agricultural systems, especially for acidic Oxisols and no-till systems. Finally, struvite production from swine wastewater can expand in specific states in the South, Southeast, and Midwest of Brazil, where the swine production is concentrated. Struvite production technology might be easily adopted and affordable for medium- to large-scale confined swine operations, which could yield some 300,000 Mg of struvite per year.

**Keywords:** swine manure, digestate, magnesium, nitrogen, nutrient management.

## INTRODUCTION

Struvite is a monoammonium phosphate of magnesium ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) with a high potential as a slow-release fertilizer; a source of phosphorus (P) as well as nitrogen (N) and magnesium (Mg). Struvite crystal major characteristics for agronomic interest are their low solubility in water and alkaline media and increasing solubility in low pH ( $<7.5$ ), and relatively high nutrient content: 12 % of P, 10 % of Mg, and 5 % of N, in its pure composition (Rahman et al., 2014). Struvite is produced by nutrient recovery (P and N) from an array of urban (sewage) and agro-industrial effluents (e.g., swine wastewater) (Muhmood et al., 2019; Hollas et al., 2021), and its commercial production is typically decentralized with units widespread in developing countries (<https://phosphorusplatform.eu/activities/p-recovery-technology-inventory>).

Struvite production has been considered one of the most sustainable technologies, based on the circular economy, to face challenges regarding P reserves and their use for conventional fertilizer production (Achilleos et al., 2022). Its importance is related to the sustainable use of P for food production. Indeed, struvite is a fertilizer obtained from nutrient recovery from wastewater, which could have a high impact on reducing the Brazilian dependency on fertilizer imports. However, its potential as a slow-release fertilizer and better use for Brazilian agricultural conditions is still unknown.

This systematic review examines global trends in struvite production and utilization as an agricultural fertilizer, with particular emphasis on evaluating Brazil's capacity to integrate swine wastewater-derived struvite into its agricultural systems. We emphasize the lack of knowledge on using struvite in tropical and subtropical soils and climate, especially on the high P adsorption capacity of these soils.

### An overview of research on struvite use as fertilizer

We exhaustively searched the leading database websites (e.g., Web of Science, Scopus, Science Direct, SciELO) and the Google Scholar website for peer-reviewed published studies using keywords such as struvite, magnesium ammonium phosphate, MAP, slow-release fertilizer, phosphorus, P recovery, P removal, and P fertilizers. We found several other reviews on the theme, focusing on the technology of P removal (e.g., Li et al., 2019a) or agronomic studies (e.g., Hertzberger et al., 2020).

Publication charts by country and year were generated from a search conducted on the Web of Science and Scopus platforms, using the terms "struvite" AND ("agriculture" OR "crop production" OR "soil fertility"). The search resulted in 302 articles (original papers and reviews), the first of which was published in 1999, with themes relating struvite to agriculture, and it showed an increase in struvite agricultural research since then (Figure 1a). The cooperation network between countries in research on using struvite as a fertilizer in agriculture is illustrated in figure 1b. The size of the nodes represents the volume of publications from each country, while the connections between them indicate international collaborations. China, the United States of America, and Germany are the leading research centers, with strong interaction with other countries, such as the United Kingdom, Canada, and Australia. In addition, European countries, such as Spain, Italy, and the Netherlands, collaborate meaningfully. The same trend was found for the "phosphorus recovery" (AND "wastewaters" AND "struvite") search topic on the database platforms (data not shown).

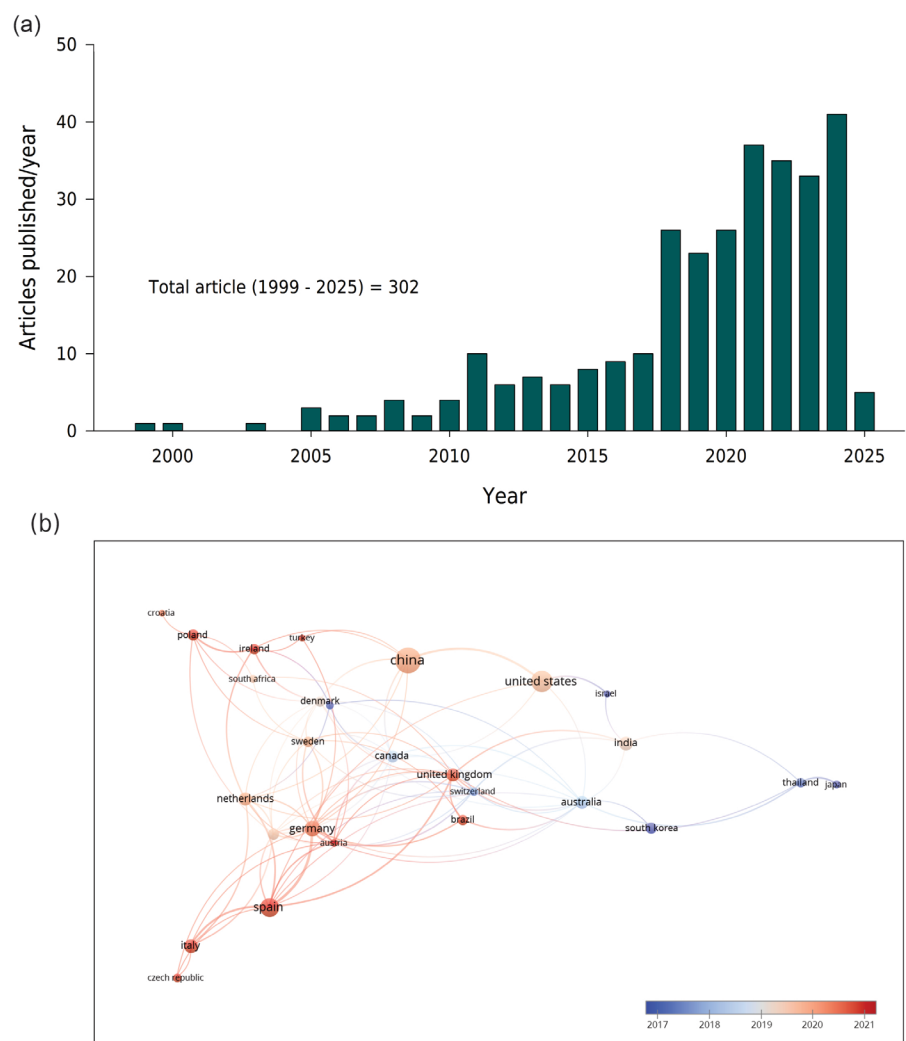
In summary, we found a sharp increase since 2015 in research on struvite, both on the technology of P removal (data not shown) and agronomic studies; however, with the low insertion of Brazil in international collaborations on the subject yet.

### Phosphorus in agriculture: an essential, limited, and strategic resource.

Phosphorus is the second most important nutrient in agriculture - nitrogen is the first. In plant metabolism and physiology, P plays a key role in the conservation and transfer of

energy, as it is a component of adenosine triphosphate (ATP), cell membrane phospholipids, and of the nucleic acids (DNA and RNA), e.g., in the ribosomal RNA (rRNA), which synthesizes the Rubisco enzyme, crucial for photosynthesis (Jin et al., 2015). Phosphorus has a relevant role in regulating plant responses to abiotic stress, such as heat, salinity, increasing CO<sub>2</sub> levels, and toxic elements, impacting the P availability for the stomata's mechanism (Khan et al., 2023). Scarcity of inorganic P (Pi) in soil solutions affects plant growth (reducing photosynthesis rate), flowering, grain filling, and fruit production (reproductive plant organs), which translates into low crop yields.

Unlike N, an element abundant in the atmosphere with a wide cycle and an intense flux through soil-biota-atmosphere due to its gaseous forms, the P cycle is tight between soil and the biota. Furthermore, mined P sources for fertilizer production are limited and nonrenewable (Thiessen et al., 2010). All the phosphate contained in conventional fertilizers comes from mined phosphate rocks, igneous or sedimentary. The P in rocks is found predominantly in the form of minerals such as apatite (Ca-phosphates), mainly fluor-apatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>) and hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) (Van Straaten, 2002). Phosphorus rocks must be milled and acidified to become commercial fertilizers with high water-soluble phosphate content.



**Figure 1.** Distribution of publications related to struvite, soil fertility, and agriculture by year (a) and research cooperation networks between countries (b), based on searches performed on the Scopus and Web of Science platforms.

Phosphate rocks (PR) scarcity has been debated in recent decades, and alarmism seems to be set apart, whereas “the static lifetime is much more likely to be of the order of hundreds or even thousands of years rather than decades” (Mew, 2024). However, Mew (2024) also considers that analysis of mineral availability is a continuously changing situation, and ecological economics principles should be inserted into the research to determine future PR feasible reserves. In addition, there is a need to reduce the enormous P loss (“from mine to fork”), and increasing recycling P and access of legacy P in soil emerge as real challenges (Köhn et al., 2018; Pavinato et al., 2020). Ulrich and Frossard (2014) have already argued that P scarcity is more of a socioeconomic and environmental problem to solve than a geological constraint. Therefore, P scarcity is controversial; at least the certainty relies on increasing global demand and price peaks of fertilizers and a few larger state-owned producers, such as Marroco (roughly 70 % of world P mines), the USA, China, and Russia (USGS, 2025). Brazil, for instance, has limited P reserves and an insufficient supply for domestic demand, leading to some 72 % of P fertilizers being imported (~8.6 million tons annually in 2023), which led the government to establish programs to reduce such external dependency (Brasil, 2023; ANDA, 2024).

### Phosphorus adsorption in tropical soils: a key problem

The predominance of acidic soils in Brazil, associated with oxidic mineralogy, mainly Fe and Al oxides, favors sorption reactions with P, significantly reducing the labile fraction of this nutrient (Parfitt, 1989; Alovisei et al., 2020). Among the macronutrients, P is the least required by crops in general, but due to its widespread deficiency in tropical soils, as well as its strong interaction with the soil matrix, it is the nutrient most often used in the fertilization of the majority of crops. In tropical regions, the intense chemical weathering during soil formation promotes acidity by releasing H<sup>+</sup>, which leads to the appearance of Al ions (toxic to plants) (Bloom et al., 2005; Barrow, 2017). As a result, there is an increase in the soil acidity and a high proportion of oxides in the clay fraction.

American continent has the highest proportion of acidic soils on a global scale, with 41 % of its soils showing acidity. In comparison, Asia, Africa, Europe and Oceania have approximately 26, 17, 10, and 6 % of their soils with pH below 5.5, respectively (Von Uexküll and Mutert, 1995). Although acidic soils are distributed throughout America, 57 % of the soils in South America are acidic, while in North America, this proportion is around 35 %. Brazil contributes significantly, accounting for 47 % of all the acidic soils in South America. Brazil, in particular, has a large part of its territory under naturally acidic soils, with some 67 % showing pH below 5.5 (Crespo-Mendes et al., 2019). The exceptions are the arid areas of northeastern Brazil and a small strip of the Pampa Gaúcho area, on the border with Uruguay. In North America, Spodosols, Entisols and Alfisols predominate, while South America is home to Oxisols and Ultisols (Von Uexküll and Mutert, 1995).

Through scientific research, Brazil has been using technologies that make it possible to cultivate on acidic soils, which in the past did not present favorable prospects for use, such as those in the Cerrado Biome (Brazilian Savannah).

### The (low) level of efficiency in the use of phosphorus sources

The main challenge in managing phosphate fertilization lies in the difficulty of reaching the critical level (CL) or sufficiency range (SR) values of P in the soil, as required by crops. This is due to the rapid adsorption of a significant part of the P applied by the functional groups of inorganic reactive particles due to the intense interaction with clay minerals. Therefore, phosphate forms high-energy covalent ionic bonds on the surface of these oxides, resulting in low availability of the nutrient. This justifies the high doses of P recommended to reach the CL or SR in the soil, which are necessary to achieve satisfactory yields. Even with these practices, it is estimated that a significant portion (>70 %) of the excess P added through fertilizers remains in the soil in forms that are not readily available to crops (Pavinato et al., 2020; El Attar et al., 2022). For annual crops,

according to Bhattacharya (2019), less than 20 % of the P applied as fertilizer is directly available to the plants in the same year of application. However, this negative effect on P availability decreases with P fertilization over time (decades) due to the saturation of the P sorption soil capacity, which improves the P fertilizing efficiency (Marchezan et al., 2023, 2024).

Forms of P found in soil are derived from orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and depend on pH. The predominant form in tropical soils is  $\text{H}_2\text{PO}_4^-$ , which is also the main chemical species absorbed by plants (De Conti et al., 2015). The high reactivity of P with the soil solid phase means that the anion  $\text{H}_2\text{PO}_4^-$  is not very susceptible to leaching losses (Tiecher et al., 2020). Due to low concentration in the soil solution, the main supply mechanism for plants is diffusion (Marschner, 2011), i.e., against a concentration gradient, thus requiring energy expenditure for its effective absorption by the roots.

Main sources of phosphate fertilizers in the country are: simple superphosphate, triple superphosphate, MAP, DAP, magnesium thermophosphate, and natural rock phosphate (domestic or imported). In addition to mineral sources, animal manure, such as digestate from anaerobic digestion, is an important source of nutrients for crops, totally or partially supplying industrialized fertilizers (Ferreira, 2022). However, the accumulation of P in soils subjected to manure application is frequently reported in the literature when high doses are applied. Establishing the dose based on technical criteria is essential to mitigate the risk of environmental contamination and to maximize the efficiency of the applied input (Brunetto et al., 2012; Guardini et al., 2012a,b; De Conti et al., 2015; Couto et al., 2018; Tiecher et al., 2020; Marchezan et al., 2023).

### Phosphorus recovery: second-generation fertilizers

We can recover N from the atmosphere by using the Harber-Bosch process (ammonia for fertilizers) or by promoting Biological Fixation (BNF) in agriculture; however, P does not follow a similar cycle. The P lost from agricultural soils, by erosion or leaching, goes down to aquatic environments and will stay there, with no viable recovery (Thiessen et al., 2010). On the other hand, highly weathered soils are prone to phosphate adsorption by iron- and aluminum-oxides, like most Brazilian soils, and prevent phosphates from leaving the system. Another problem is that it is not easy to recover P through plants or microorganisms, despite researchers' continuous efforts to find ways to do so with good agricultural practices and new fertilizing technologies (Khan et al., 2023), and even by using bio-products based on phosphate-solubilizing bacteria (Oliveira-Paiva et al., 2021; Souza et al., 2023).

On the other hand, animal manure has an enormous reservoir of P and other important nutrients such as N and potassium (K). Most nutrients ingested by cattle, swine, and poultry are excreted; for P, the feed efficiency is only 10 %. The amount of these nutrients in the manure reservoir is nearly equal to the amount of nutrients applied as fertilizers in agriculture around the world. Data show 26 Tg year<sup>-1</sup> of P in manure and 23 Tg year<sup>-1</sup> of P in fertilizers, and 139 Tg year<sup>-1</sup> of N in manure against 103 Tg year<sup>-1</sup> in fertilizers (Bouwman et al., 2013). The greater and better use of nutrients from animal manure in agriculture represents the most promising scenario to reduce the global surplus of P and N flux into the environment and its harmful effects (Bouwman et al., 2013). In Brazil, animal manure, mainly swine and poultry manure, is currently recycled to croplands, representing nearly 266 Gg of P by 2015, and the estimated increase is close to 400 Gg of P by the year 2050 (Withers et al., 2018).

Paths to sustainable P use in agriculture will involve more effective ways of recovering this nutrient from animal manure. The fact is that P is a limited resource and will become a limiting factor of food production due to its scarcity and/or the rise of fertilizer prices. Brazilian food production is highly vulnerable to this scenario because of its high dependency on fertilizer imports, and a strategic analysis points to the secondary P

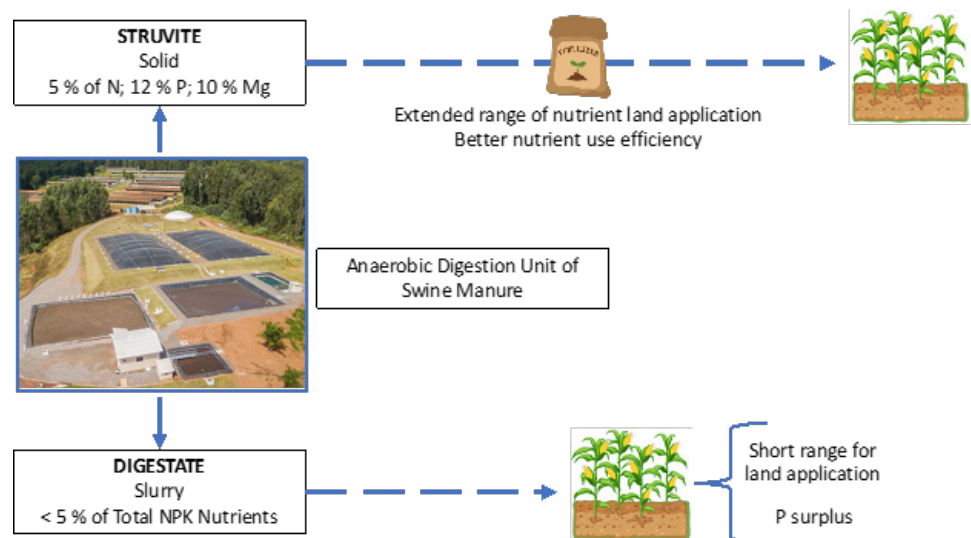
resources providing up to 20 % of crop P demand by 2050 with investments in P recovery technologies (Withers et al., 2018).

Direct manure application to soil is the easiest way of using it in agriculture and is widely used worldwide - it goes back to the origins of agriculture. However, the current scale of confined animal feeding operations (CAFO) and the characteristics of manure (such as low relative content of nutrients) compromise this procedure's cost-effectiveness due to transport and distribution costs. New technologies have sought to concentrate those nutrients, such as struvite mineral and calcium phosphates. Phosphorus fertilizers produced from animal manure (e.g., swine wastewater) are called second-generation P fertilizers (Hollas et al., 2021). The higher nutrient (phosphate) content of these alternative nutrient sources increases their economic potential in agriculture and, as a consequence, it increases the distance of their use in crops compared to raw manure or digestate (Figure 2).

## Struvite and its production

### Global struvite production

Full-scale operational nutrient recovery facilities have been increasing in recent years, mostly in developed countries, and installed on liquid sludge streams. Struvite crystallization is the most adopted among the technologies employed for P recovery. According to Shaddel et al. (2019), up until 2019, over 80 plants for struvite recovery were in operation worldwide, including more than 60 plants in municipal wastewater treatment plants. These plants are located in countries or regions with a P surplus, often due to intensive livestock production and limited agricultural area for land application of wastewater, or regions with high population density. Shaddel et al. (2019) highlighted the successful strategies adopted in Japan since the 1980s to establish P recovery through a collaboration between industry, academia and the government to create business models and market development strategies for producing struvite or calcium phosphate from wastewater. In the European Union, the estimated amount of struvite produced in 2020 was 9,784-12,057 Mg, corresponding to 1,095-1,353 Mg of P equivalent (Muys et al., 2021).



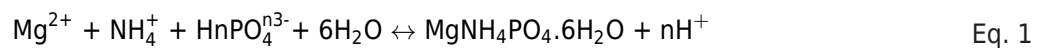
**Figure 2.** Diagram showing how phosphorus and nitrogen recovery as struvite delivers a solid, dry, and higher-nutrient-content product than swine manure or digestate. This enhances the range of nutrient distribution and nutrient use efficiency, thereby reducing water and soil contamination.

Struvite production has received significant attention for its various uses, including the prevention of excessive nutrient enrichment in surface waters and the production of bioavailable fertilizers to address the ongoing shortage of P-based resources, for food additives, chemical agents, structural products, fire retardant agents, and as an adsorbent material (Li et al., 2019b). The noteworthy advantage of struvite crystallization lies in the commercial potential of the recovered product as a second-generation P resource (Hollas et al., 2021; Wang et al., 2023a; Guan et al., 2023).

Struvite precipitation has proven to be an effective N and P recovery technology for various wastewater types, including semiconductor wastewater (Ryu et al., 2008), swine wastewater (Chu et al., 2018; Ryu et al., 2020; Zhang et al., 2020; Ha et al., 2023), domestic wastewater (Hallas et al., 2019; Dai et al., 2023), urine (Krishnamoorthy et al., 2020, 2021; Tan et al., 2021), spent firebrick gravel from the steel industry (Li et al., 2022), tannery sludge (Tünay et al., 2004; Yang et al., 2023) and slaughterhouse wastewater (Kabdaşlı et al., 2009). This resource recovery positively contributes to the global balance of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ , enhances the economics of wastewater treatment, promotes sustainable technologies, and drives the circular economy (Wu and Vaneekhaute, 2022).

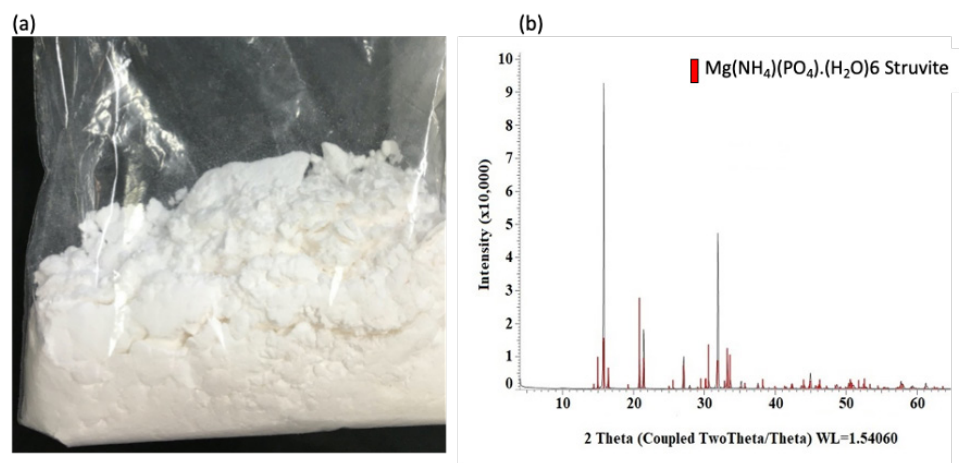
### Chemical and mineralogical characteristics of struvite

Magnesium ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), commonly known as struvite, is a white mineral generated in supersaturated solutions of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  (Equation 1). Pure struvite generally exists in powder (Figure 3a) form, but can also exist in single-crystal or gel forms (Guan et al., 2023).



Crystal formation is a two-step process involving nucleation and crystal growth. Supersaturation primarily controls the induction period preceding the appearance of the first crystal nuclei (primary nucleation), the formation of nuclei in the presence of other struvite crystals (secondary nucleation). Nucleation is crucial, especially in the absence of seeds in the solution (Kabdazsli et al., 2006).

Crystal formation (i.e., nucleation) usually occurs spontaneously (homogeneous nucleation) or may be aided by the presence of suitable nuclei, which may be solid impurities in suspension or on tube walls (heterogeneous nucleation) (Doyle and Parsons, 2002).

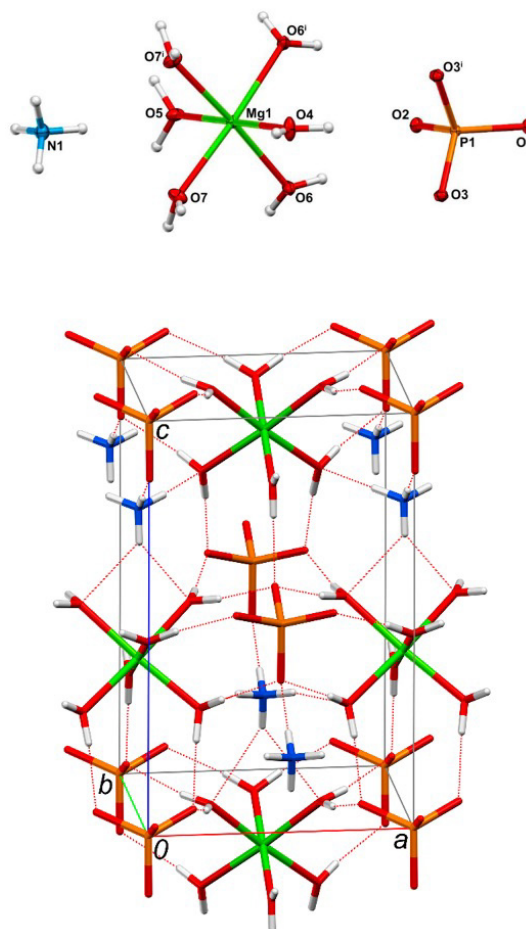


**Figure 3.** Picture of pure struvite obtained through precipitation of commercial reagents, after drying (a); X-Ray Diffraction pattern of struvite crystals (b).

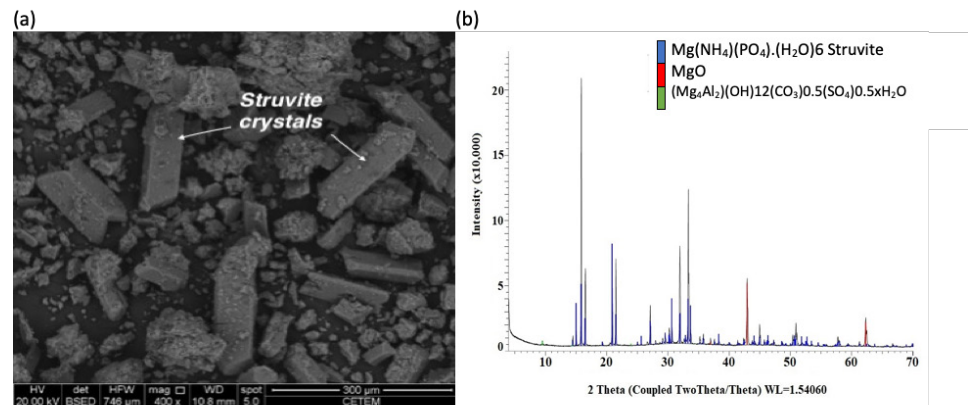
Struvite crystallization process, from nucleation to crystal growth, is complex – it is controlled by physicochemical factors such as pH, saturation reaction, temperature, the existence of various ions ( $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ), silicates, oxalates, and organic ions (Muryanto and Bayuseno, 2014; Yan and Shih, 2016; Tansel et al., 2018; Gao et al., 2023) as well as total suspended solids (Ping et al., 2016). Impurities in the solution affect the growth rates of crystalline compounds, blocking potential crystal formation sites, inhibiting crystal size increase, affecting crystal size, and causing a decrease in the crystallization rate of struvite and the kinetic rate constant with increasing heavy metal ion concentration (Le Corre et al., 2005; Chen et al., 2023).

Crystals formed may contain struvite and other solids, depending on the variety and concentration of ions present in the aqueous systems and solution pH. Crystals can contain the same three ions as struvite ( $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$ ) but in different proportions, or they can form by substituting other ions in the solution. Other ions can replace  $\text{NH}_4^+$  (e.g.,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) or  $\text{Mg}^{2+}$  (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ), resulting in crystals similar in appearance to struvite but with different compositions (Ravikumar et al., 2010).

Geometric structure of the struvite crystal was precisely demonstrated and illustrated by Prywer et al. (2019) (Figure 4), and consists of  $\text{PO}_4^{3-}$  (tetrahedral),  $\text{Mg}^{2+}$  ( $6\text{H}_2\text{O}$ ) (octahedral), and  $\text{NH}_4^+$  (tetrahedral) groups held together by hydrogen bonds. Struvite crystals have a distinct orthorhombic structure and can be identified by X-Ray Diffraction (XRD), combining the intensity and position of peaks produced with a database for the crystal structure, and Scanning Electron Microscopy (SEM) (Tansel et al., 2018) (Figure 3b and Figure 5).



**Figure 4.** Structure of struvite crystal containing  $\text{PO}_4^{3-}$  anions, hexa- $\text{Mg}(\text{H}_2\text{O})^{2+}$  and  $\text{NH}_4^+$  cations connected within a three-dimensional hydrogen-bonded network. Source: Prywer et al. (2019).



**Figure 5.** Struvite obtained from digestate from anaerobic digestion of swine manure. Scanning electron microscope (SEM) image at 400× mag indicating the presence of struvite crystals (a); X-Ray Diffraction pattern of precipitated struvite (b).

Formation of other minerals, such as magnesite, newberyite, and dolomite, is typically lower due to inadequate pH values or low precipitation rates (Pastor et al., 2010). However, in natural environments, the occurrence of struvite has been associated with newberyite  $\text{Mg}(\text{PO}_3\text{OH}) \cdot 3(\text{H}_2\text{O})$ , hannayite  $(\text{NH}_4)_2\text{Mg}_3\text{H}_4(\text{PO}_4)_4 \cdot 8(\text{H}_2\text{O})$ , brushite  $\text{CaHPO}_4 \cdot 2(\text{H}_2\text{O})$ , and stercorite  $\text{NaNH}_4\text{HPO}_4 \cdot 4(\text{H}_2\text{O})$  (Mineral Data, 2001).

The pH range at which struvite can precipitate is between 7 and 11 (Doyle and Parsons, 2002). Alkaline pH increases the ionic activity of the product due to supersaturation of the solution, favoring struvite crystallization. The metastable range of struvite precipitation is between pH 8 and 10. A pH exceeding 11 is unfavorable due to side reactions forming  $\text{Mg}(\text{OH})_2$  and the evolution of free  $\text{NH}_3$ , reducing the availability of  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  ions for struvite formation. Such a change results in the formation of other phosphate compounds alongside struvite, such as  $\text{Mg}_3\text{PO}_4$  and  $\text{Mg}(\text{OH})_2$  (Bayuseno et al., 2020).

The pH can influence both the constituents of the solution and the morphology and size of the crystals formed, as well as the induction time of crystal growth. At pH values of 8.7 and 8.5, crystal growth begins faster than at higher pH values (Moulessehouli et al., 2017). However, optimal pH values depend on wastewater composition, with different wastewater streams having different optimal pH values, mainly as a function of  $\text{Ca}:\text{Mg}:\text{P}:\text{NH}_4^+$  ratios (Hao et al., 2008). During the reaction process, a drop in pH is observed, a characteristic of the rate at which the first struvite crystals form, according to equation 1, with the production of  $\text{H}^+$ , and is linked to the rate of struvite formation, influencing the quality of the crystals formed (Williams, 1999).

Regarding the temperature for struvite formation, Zeng et al. (2006) recommended an operating temperature between 15 and 35 °C. For the induction time, temperatures above 20 °C have no effect, but they significantly influence the supersaturation coefficient when the temperature increases from 14.5 to 35 °C (Ben Moussa et al., 2011). Struvite morphologies present a well-faceted structure with a bipyramidal appearance at temperatures of 25 and 40 °C, while at 33 °C, a combination of different morphologies is observed (González-Morales et al., 2021). The average particle size of crystals increases with the temperature rising from 20 to 60 °C (Polat and Sayan, 2019). Given their slow-release properties, these crystals are considered potential fertilizers, suitable for use in moderately alkaline and acidic soils (Yan and Shih, 2016).

### Potential of struvite production from swine wastewater

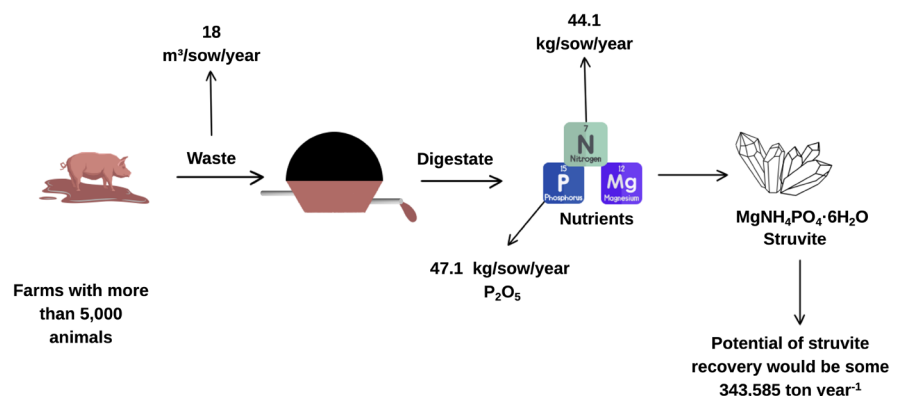
Brazil ranks 4th in swine and swine product exportation and production worldwide. This economic activity is mainly concentrated in the states of Santa Catarina, Rio Grande do Sul, Paraná, and Minas Gerais, which were responsible for some 81 % of the slaughtered animals in 2022 (ABPA, 2023). Swine manure shows considerable concentration of organic

matter and nutrients (N, P, and K) and, consequently, huge amounts of wastewater rich in these components are generated and remain concentrated in the main swine-producing states (Kunz et al., 2019). Problems with P surplus in soil are already reported in Santa Catarina and other regions in Brazil where swine production is concentrated (Gatiboni et al., 2015; 2020). In this sense, adopting a P recovery technology, i.e., struvite, before land application of wastewater is crucial.

Considering the total swine production in Brazil and, consequently, the volume of swine wastewater produced, this effluent represents an interesting source of P and N for struvite production. However, due to the characteristics of farms in terms of the number of animals and production systems, implementing treatment facilities for nutrient recovery is not economically viable in all of them. Additionally, it has to be considered that a P surplus is not a reality in all locations, and on many farms, there is land available for swine wastewater use in the soil. Therefore, to make a more realistic estimate of the second-generation P recovery potential through struvite production in Brazil, we considered farms with more than 5,000 animals in the states of Santa Catarina, Rio Grande do Sul, Paraná, Minas Gerais, Goiás, Mato Grosso, Mato Grosso do Sul and São Paulo. The amount of struvite production was calculated considering the concentration of P and ammoniacal N in swine wastewater, the volume of wastewater produced per swine per year, and the total number of swine, as described by Miele and Almeida (2023). In this scenario, the potential of struvite recovery would be some 343,585 Mg year<sup>-1</sup>. However, this production rate may depend on the concentration of available P and Mg, the effect of contents interfering in wastewater, and the struvite precipitation technology applied. The scheme presented in figure 6 highlights the potential scenario for struvite production in Brazil.

### Struvite production associated with anaerobic digestion

Considering full-scale struvite plants in operation worldwide, three basic technologies of struvite precipitation processes are highlighted: 1) struvite production from waste activated sludge (WAS) or digestate from anaerobic digestion in continuous stirred tank reactors (CSTR); 2) precipitation of struvite from dewatering liquids of the WAS digestate after a solid-liquid separation step; 3) from agro-industrial wastewater treatment (i.e., potato processing, dairy) (Muys et al., 2021). In the case of animal production (i.e., swine wastewater), anaerobic digestion is a valuable technology for eliminating biodegradable pollutants and stabilizing farming waste while producing bioenergy through biogas (Lourinho et al., 2020; Hollas et al., 2023). However, anaerobically digested swine wastewater (digestate) represents a complex system containing an array of inorganic ions (Ca, Cu, Zn, Cd, Pb, Cr, etc.), organic matter (humic acids, extracellular polymers, etc.), in addition to constitutive crystalline ions (NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup> and Mg<sup>2+</sup>) and trace elements (cations) that affect the struvite crystallization process (Guan et al., 2021; Wang et al., 2023b).



**Figure 6.** Scheme with the estimation of the second-generation P recovery potential through struvite production in Brazil, only considering farms with more than 5,000 animals in the states of Santa Catarina, Rio Grande do Sul, Paraná, Minas Gerais, Goiás, Mato Grosso, Mato Grosso do Sul, and São Paulo.

Typically, anaerobically digested swine wastewater contains high concentrations of P, N, Mg, and Ca (Liu et al., 2011). Producing struvite from these wastewaters is advantageous as higher concentrations of N and Mg favor the formation of pure struvite (Li et al., 2017). Compared to raw swine manure, during the anaerobic digestion process, most of the organic matter is degraded, releasing P to its inorganic ions,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , depending on digestate pH; and N-organic to  $\text{NH}_4^+$ . Therefore, the production of struvite from digestate is more advantageous than its production from raw manure, leading to higher P and N recovery rates (Kunz et al., 2019). Additionally, the production of struvite after anaerobic digestion is a sustainable approach since this combination enables the recovery of energy (anaerobic digestion) and nutrients (mainly P and N) as demonstrated by studies on life cycle analyses (Hollas et al., 2021).

Despite these advantages, researchers highlight the challenge of recovering struvite from anaerobically digested swine wastewater due to the molar proportions of calcium ( $\text{Ca}^{2+}$ ) dissolved in relation to its component ions (Ha et al., 2023). Another challenge for P recovery in swine wastewater involves a preliminary P-dissolution step followed by separating particulate organic matter (OM). Subsequent steps include the precipitation and filtration of struvite crystals. Successfully developing the process at an industrial scale relies on controlling precipitation mechanisms to obtain products with high added value: large struvite crystals that are easier to harvest and handle (Capdevielle et al., 2016).

Nutrient recovery from swine waste using the struvite crystal formation method provides an alternative for nutrient recovery and waste reduction, offering a promising future for the economic and environmental sustainability of agricultural processes. It is also a green marketing tool in the fertilizer and wastewater treatment industry (Nagarajan et al., 2023).

## Struvite based-fertilizer

### *Nutrient content, trace elements, pH, and salt index*

Phosphorus content of struvite minerals is comparable to soluble fertilizers and much higher than alternative P sources, such as phosphate rocks, manure and composts. Also, struvite has higher N content and much higher Mg content than organic fertilizers. Highly-pure commercial struvite-based fertilizers (Cristal Green®) typically have 12.2-12.9 % of P (~29 %  $\text{P}_2\text{O}_5$ ), 5.0-5.7 % of N and 9.5-10 % of Mg, which is similar to struvite obtained in laboratory conditions (Bhuiyan et al., 2008; Latifian et al., 2012; Degryse et al., 2017). Thus, its nutrient content can vary due to production conditions (Table 1) and it might also alter some chemical properties such as solubility. A much higher nutrient content (8.8 % N; 17.8 % P; 23.7 % Mg) was reported for a struvite obtained from anaerobically digested sewage sludge (AirPress® process), which also included C (13.9 %) and some Ca (0.8 %) (Meyer et al., 2018).

It may be expected that struvite-based fertilizers with high purity will show the typical nutrient content; meanwhile non-pure products might contain “impurities” like organic carbon, K and Ca ions (i.e., calcium phosphates), MgO and other elements (Achat et al., 2014; Rech et al., 2019). As Achat et al. (2014) reported, a recycled-P product from swine manure showed 12-38 % of struvite, 15-35 % of Ca-P, and 47-57 % of MgO. Formation of other magnesium phosphates, e.g.,  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  (newberyite), can occur during the crystallization process and post-production, altering both the general solubility and final nutrient content of the product (Bhuiyan et al., 2008). Also, excessive Mg during struvite formation (in lab conditions) reduced the P and N total content to 7.4 and 3.3 %, respectively, meanwhile Mg increased to 14.6 % (Degryse et al., 2017). Applied production technologies will drive the quality of the final struvite-based fertilizer. Granules of struvite-based fertilizers show alkaline pH to neutral, i.e., typically 7 to 10, and an expected pH around 9 for pure struvite (Latifian et al., 2012; Degryse et al., 2017). In contrast to soluble phosphate fertilizers, struvite shows an alkaline pH and low salt indexes (S.I.).

**Table 1.** The nutrient composition variation of several struvite products

| Reference              | Composition |          |           |                         | Source                                 | Estimated purity |
|------------------------|-------------|----------|-----------|-------------------------|----------------------------------------|------------------|
|                        | N           | P        | Mg        | Others                  |                                        |                  |
|                        | %           |          |           |                         |                                        | %                |
| Bhuiyan et al. (2008)  | 5.7         | 12.6     | 9.9       | -                       | Theoretical value for pure struvite    | 100              |
|                        | 5.5         | 12.7     | 9.7       | -                       | Synthetic solution                     | >99              |
| Gell et al. (2011)     | 5.3         | 11.6     | 14.0      | K, Ca, Fe, Na, S        | Urine                                  | -                |
|                        | 5.3         | 11.9     | 10.7      | K, Ca, Fe, Na, S        | Sewage wastewater                      | -                |
| Latifian et al. (2012) | 5.6         | 13.1     | 9.6       | -                       | Municipal wastewater, Sweden           | -                |
|                        | 5.7         | 12.0     | 9.5       | -                       | Municipal wastewater, Canada           | -                |
| Achat et al. (2014)    | 10.2        | 22.6     | 17.7      | -                       | Synthetic solution (Sigma Aldrich®).   | >99              |
|                        | 1.2-3.7     | 7.8-12.4 | 22.5-26.2 | Ca-P, MgO               | Swine wastewater                       | *                |
| Uysal et al. (2014)    | 3.5         | 10.8     | 7.97      | K, Ca                   | Anaerobic effluent from yeast industry | -                |
| Ryu and Lee (2016)     | 14.8        | 15.6     | 10.2      | C <sup>†</sup> , K, Cl  | Swine wastewater                       | *                |
| Degryse et al. (2017)  | 5.0         | 12.2     | 10.0      | -                       | Cristal Green® fertilizer              | >99              |
|                        | 5.6         | 12.5     | 10.8      | -                       | Synthetic solution                     | >99              |
|                        | 4.9         | 10.8     | 14.8      | Brucite                 | Synthetic solution with MgO excess     | -                |
|                        | 3.3         | 7.4      | 14.6      | Brucite                 | Synthetic solution with MgO excess     | -                |
| Meyer et al. (2018)    | 8.8         | 17.8     | 23.7      | C <sup>†</sup> , Ca, Fe | Anaerobically digested sewage sludge   | *                |

\* Recycled P products may contain struvite and other minerals, such as Ca-P, and organic matter; <sup>†</sup> 20.0 %; \* 13.9 %.

For example, a commercial NPK fertilizer showed pH = 5.9 and S.I. = 54.3, whereas struvite showed pH = 9 and S.I. = 0.59 (Latifian et al., 2012). Commercial struvite-based fertilizers show S.I. = 10 (Rech et al., 2019). Thus, a negative effect of the application of struvite on soil regarding crop seeds and roots and even salt accumulation in soil is not expected (Latifian et al., 2012).

Struvite-based fertilizers are products with low content or absence of contaminants such as heavy metals (e.g., Cd, Cr, Cu, Ni, Pb, Zn), pathogens (*E. coli*, fecal coliforms and Salmonella), and emerging contaminants, i.e., limiting factors for animal manure and biosolids (sewage sludge) used as soil amendments and P sources (Pepper et al., 2006; Sidhu and Tozze et al., 2009; Clarke and Smith, 2011; Sommer et al., 2013; Benedet et al., 2020; Furtado and Silva et al., 2022). For example, struvite obtained from wastewater treatment systems exhibits a lower cadmium (Cd) content *per* kg of delivered P than commercial fertilizers, at approximately 0.16 mg kg<sup>-1</sup>, compared to 79.6 mg kg<sup>-1</sup>. Additionally, it shows a lower Cd content than the vast majority of P rock reserves (Latifian et al., 2012). Also, Rahman et al. (2014), Ahmed et al. (2018), and Muhmood et al. (2019) show data on the low heavy metal content of struvite-based fertilizers.

### Struvite solubility

The solubility of struvite is weakly affected by temperature, but strongly affected by pH solutions, i.e., increasing solubility from alkaline to acid, pH <9 (Bhuiyan et al., 2007; Talboys et al., 2016). Slightly soluble in water, struvite is highly soluble in citric acid and

other organic acid anions, e.g., malate, acetate, oxalate, which sharply increase both initial P rate dissolution and the equilibrium of P concentration (Talboys et al., 2016). Struvite showed 4.4 and 94 % of P solubility in water and citric acid, respectively, whereas phosphate rock (hydroxyapatite) showed a solubility of only 26 % in citric acid and virtually no solubility in water (Meyer et al., 2019). Using struvite granules, Talboys et al. (2016) found that the equilibrium of P concentration was reached with less than 1 % of P in struvite granules, which shows its slow-release property. Struvite solubility (initial rate and equilibrium of P concentration) is also strongly inhibited in the presence of increasing initial  $[\text{PO}_4^{3-}]$ , which might be relevant in mix fertilization with soluble P fertilizers. The other counter-ions,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  have no significant effect on struvite solubility (Talboys et al., 2016).

Although slightly water-soluble, struvite contains all P readily available as extractable for resin and  $\text{NaHCO}_3$  extractable P ( $\text{P}_i$  and  $\text{P}_o$ ), which was a better indicator for struvite's relative fertilizing effectiveness compared to water-soluble P source and phosphate rocks (hydroxyapatite and brushite) (Meyer et al., 2019). In fact, water ( $\text{P}_w$ ) and citric acid ( $\text{P}_{\text{CitAcid}}$ ) soluble P were not good indicators of the relative fertilizer effectiveness (found through  $^{33}\text{P}$  isotope dilution method; *Lolium multiflorum*; greenhouse) of struvite as resin-P and  $\text{NaHCO}_3$ -P (sequential extraction) which showed a higher, positive and significant correlation with plant response in both acidic and calcareous soils (Meyer et al., 2019). Thus, while  $\text{P}_w$  underestimates and  $\text{P}_{\text{CitAcid}}$  overestimates P solubility from struvite-based fertilizers, resin- and  $\text{NaHCO}_3$ -P allowed for a more accurate assessment of the potential of struvite as a P source.

Different formulas for struvite-based fertilizers (granule or pellet mixture with binders) may affect solubility. The slow-releasing property (in distilled water) of struvite was demonstrated, for example, by Latifian et al. (2012) who found the total N, P, and Mg released in the range of 9.6-23.2, 8.4-26.7 and 11.3-32.6 %, respectively, depending on the formulation (pellets with adjuvants), whereas for NPK fertilizers, more than 50 % of the nutrients were released after just one day. For example, the excessive Mg during struvite formation (in lab conditions) reduced the P and N total content to 7.4 and 3.3 %, respectively, while Mg increased to 14.6 % (Degryse et al., 2017).

### Struvite P diffusion in soil

Struvite diffusion in soil has been demonstrated to be affected by particle size (granule  $\times$  powder), base excess, and soil pH. Studies have shown a sharp decrease in struvite dissolution when it is granulated as a fertilizer compared to its powder form (Talboys et al., 2016; Degryse et al., 2017; Everaert et al., 2017). For instance, Talboys et al. (2016) found intact granules of struvite undissolved after 90 days of a pot experiment with spring wheat (*Triticum aestivum*), when only 18 to 36 % of the mass of granules dissolved completely. On the other hand, when powder struvite is mixed with soil, it dissolves more quickly. However, the dissolution of struvite granules (mass) was found to be much lower when struvite has a base excess (8 %) and when it reacts in alkaline soils (2.1 %) (Degryse et al., 2017).

Considering the pH effect on struvite crystals' solubility, soil pH may affect struvite dissolution in the same direction, i.e., acidic > alkaline. However, soil pH affects the dissolution of granulated struvite much more than fine powder struvite, which may explain conflicting results found in the literature. Some authors found no influence of soil pH on struvite effectiveness as a fertilizer (Achat et al., 2014) and even in moderately alkaline soil, i.e., limed to pH 7.6 (Massey et al., 2009). But, struvite had its fertilizing effectiveness reduced by nearly 40 % in calcareous soils (pH 7.7, total  $\text{CaCO}_3$  18 g  $\text{kg}^{-1}$ ) (Meyer et al., 2018). Nevertheless, in these studies, only powdered struvite mixed with soil was used. When granulated struvite was applied to the soil (incubation or pot experiments), major differences in dissolution rate and/or fertilizing effectiveness

were found in a wide range of pH values (acidic to alkaline soils). For instance, Degryse et al. (2017) found a dissolution rate of  $0.43 \text{ mg day}^{-1}$  in acidic soils (pH 5.9) and a low,  $0.03 \text{ mg day}^{-1}$ , in alkaline soils (pH 8.5) with granulate struvite. The increasing soil:fertilizer ratio contact when struvite is ground and mixed to soil leads to a quick dissolution of the crystals; however, in granular form the rate-limiting process is the diffusion of P from the particle surface into the soil (Degryse et al., 2017). Indeed, struvite consists of two P pools, i.e., water extractable P (<5 %) and readily available P (>90 %) (Meyer et al., 2018). Thus, the dissolution rate of the struvite granule depends on soil pH, whilst the fine ground (and well mixed in soil) struvite may dissolve quickly -- even in slightly alkaline soils (pH ~7.5).

### ***Struvite-P adsorption in Oxisols***

Studies are scarce on struvite in Oxisols, typically found in tropical and subtropical climates -- these represent most of the agricultural lands in Brazil. For instance, in a recent literature review, only 21 % of struvite observations (42) were in acidic soils (pH <6), and none of those soils were in Brazil (Hertzberger et al., 2020). Oxisols are characterized by strong P adsorption due to high levels of iron and aluminum oxides associated with low soil pH (<5). Such effect reduces the fertilizing effectiveness of any P source for crops, and liming is the regular agricultural practice used to partially overcome this soil constraint. Thus, very little is known about the behavior and efficiency of struvite-based fertilizers in Oxisols, and no information was found for Brazilian soils.

Struvite apparent dissolution is highly influenced by clay content in acidic soils (Gu et al., 2021). Iron- and aluminum-oxides comprise a relevant part of the clay fraction in Oxisols, which is likely related to the P-adsorption effect on struvite's apparent dissolution. Besides, Gu et al. (2021) also found during an acid soil test (Melich-3, pH <2.7), by SEM, a deposition of Al and Si from the soil on struvite mineral surfaces, which might inhibit its dissolution. As for soluble P sources, the content of clay (with a high content of oxides) will reduce struvite apparent dissolution in soils.

Nevertheless, unlike soluble P fertilizers (i.e., MAP), granulated struvite showed an almost linear and constant P dissolution in a P diffusion visual method in plates with different soils (Degryse and McLaughlin, 2014), including an Oxisol (Everaert et al., 2017). Phosphorus adsorption starts after one day of P-fertilizer dissolution and strongly affects all fertilizers, although different P dissolution behaviors were observed. Struvite had a slower P dissolution than MAP over a 100-day test -- the former had a sharp decrease in P diffusion after seven days, likely due to the P adsorption effect. Another effect of struvite in soil was the increase of pH around the fertilizer granule (e.g., 5.1 to 6.0, <8 mm in diameter) (Everaert et al., 2017). In addition, the release of  $\text{Mg}^{2+}$  cation might result in a liming effect that partially prevents P sorption around the struvite granule. However, the following pot test (42 days, wheat) showed a poor fertilizing effectiveness of granulate struvite compared to granulate MAP in the strong P-sorption soil (Everaert et al., 2017). That pot test was carried out in a pH below the regular agricultural range, i.e., minimally appropriate to crops (5.5 to 6.5). Therefore, the hypothesis that struvite-P could be less adsorbed by Fe- and Al-oxides along a year of cropping cycles should be tested. Investigation in Brazilian Oxisols considering levels of clay content and across a range of agricultural pH values (limed soils) would be extremely valuable.

### ***Plant response, P uptake, fertilizer effectiveness***

Crop responses to struvite fertilizers have been reported as quite variable -- most of these data come from greenhouse experiments, and field research representing less than 10 % of these studies (Ahmed et al., 2018; Huygens and Saveyn, 2018; Hertzberger et al., 2020). The reason for such variability of crop responses can be found in an array of factors such as (a) granulate or powder struvite applied to the soil; (b) experiment duration and soil volume; (c) soil pH; (d) crop-specific root exudation; (e) soil P level

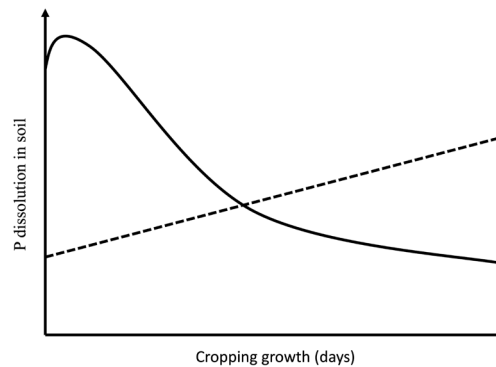
and P application rates; (f) limited N availability of struvite (Hertzberger et al., 2020). Responses of a variety of crops have been studied, such as grains, legumes, grasses, vegetables, and oilseeds, with a predominance of corn and small grains (e.g., wheat) and above ground biomass (dry matter) is the most commonly reported parameter - very few studies report grain yields (e.g., Talboys et al., 2016).

A comprehensive review and meta-analysis was performed by Hertzberger et al. (2020), which shows a similar crop response of struvite to water-soluble P fertilizers (ammonium phosphates and superphosphates) and an increase of crop response under soils with low pH, i.e., <6.0, decreasing strongly in alkaline soils (pH >7). This “similar crop response” means a response ratio of above-ground biomass around 0.94 (field studies) and 0.91 (greenhouse studies) in comparison to the conventional phosphates considered (i.e., values were significantly different from 1.00 at  $p < 0.05$ ). However, no significant difference was found for P concentration and P uptake across field or greenhouse experiments. There was a greater variability in greenhouse data than for field experiments and, according to Hertzberger et al. (2020), much of this variability may be attributed to a combination of factors, such as experiment duration/soil volume ratio; high soil P tests and excessive P doses (overestimation), and N limitation from large proportions of applied N derived from struvite (underestimation). In sum, crop responses to struvite fertilization might be slightly lower (some 10 %) or equal to conventional P fertilizers. Good crop performance would depend on soil type, crop species, and the tuning of management practices.

It is believed that struvite is not able to supply crops early P demand due to its slow solubility - thus, mixtures of water-soluble P sources with struvite have been tested (Talboys et al., 2016; Everaert et al., 2017). Talboys et al. (2016) found similar (not statistically different) in wheat grain yield, P uptake, and P recovery at harvest (90-day, pot) comparing granulate struvite with triple-phosphate (TSP). However, TSP treatment produced more grain heads ( $p < 0.05$ ). In a shorter pot experiment (36-day) there was a significant reduction (up to 39 %) of early plant P uptake compared with DAP fertilizers. Struvite granules did not dissolve completely after 90-days, with 66 to 82 % of the total initial mass of struvite remaining. Actually, considering this undissolved struvite, the yield of the 90-day pot experiment was reached with less P dissolved. In this case, the apparent wheat struvite P recovery increased from 11 to 38 % against 13 % from TSP (Talboys et al., 2016). Comparing three types of struvite against TSP, Rech et al. (2019) also found a relatively high P use efficiency (up to 80 % for soybean), although their findings also showed a lesser dry matter yield (38-day) with struvite due to an insufficient P supply in early plant growth.

In addition, to overcome the lack of early P supply to the crop by struvite, different struvite DAP mixtures were tested (36-day, pot), where mixtures with more than 20 % of struvite granules showed a reduction in plant P uptake (Talboys et al., 2016). Despite the need for more trials in different conditions (soil, crop, and fertilizers), the combination of struvite and conventional fertilizers seems to have the potential to overcome the deficiency of P supplied by struvite granules in the early days of cropping and might become an efficient agronomic practice. Also, Kokulan et al. (2024), using struvite blended with MAP (25/75 %) in a two-year field experiment, found grain yields statistically similar to those of MAP treatment, which exhibited a greater vulnerability to P losses (runoff and leaching).

Crop responses for granulated struvite might be lower compared to powder struvite, which dissolves faster in soil, and a high level of undissolved granules may also result in a poor crop response (Degryse et al., 2017; Everaert et al., 2017) (Figure 7). On the other hand, the low dissolution of granulated struvite may lead to a greater residual effect for subsequent cropping than soluble P sources (Talboys et al., 2016; Everaert et al., 2017; Rech et al., 2019). Although many authors mention the residual effect of struvite, none of the studies had really focused on measuring the residual effect of struvite in a cropping sequence.



**Figure 7.** Theoretical P dissolution in soil over the cropping growth of water soluble P fertilizer (dashed line) and struvite-based fertilizer (dotted dash). Calibrated mixing of water-soluble phosphorus fertilizer and the slow-release struvite fertilizer would be the key strategy to reach more accurate plant demand and efficient phosphorus use.

A higher crop response may be expected for plants with high levels of organic acids exuded from their roots. This was true for spring wheat (*T. aestivum*) vs. buckwheat (*F. esculentum*), low and high level exudation species, respectively. Buckwheat was able to mobilize three times more struvite-P in a 30-day pot experiment (Talboys et al., 2016). Thus, differences in P struvite mobilization can be expected among different plant species, for instance, between grasses vs. legumes; annual vs. perennial; and short vs. long crops. Plant species with a higher capacity for soil P mobilization may respond better to struvite.

Innovative struvite-based fertilizer formulas can also help to enhance struvite fertilizer effectiveness as demonstrated by Valle et al. (2022), who tested fertilizers containing a polysulfide matrix (PS) with dispersed struvite (St) and found superior biomass compared to a reference of triple superphosphate (TSP) with ammonium sulfate (AS), with similar P uptake efficiency (11 – 14 %). In contrast with Rech et al. (2019), who found a greater root expansion in treatments with TSP than with struvite, the findings of Valle et al. (2022) showed a higher proliferation of second-order lateral roots in response to struvite ongoing P delivery and higher sulfur uptake efficiency (22 % against only 8 % from TSP/AS). Thus, a window of possibilities regarding struvite-based fertilizer different formulas (e.g., Valle et al., 2021) designed to specific crops and soil type can still be explored.

In fact, crop response to struvite-based fertilizers depends on complex interactions of factors such as soil pH-dependent solubility, granule size-dependent dissolution, clay content of soil (i.e., the effect of oxides adsorption), crop-specific interactions, and limited availability of struvite-derived N. The best crop response to struvite based-fertilizers will be reached only with exhaustive and appropriate experiments under Brazilian agricultural conditions, which are also quite variable in climate and soil type (Table 2). Also, there is an array of possibilities of new formulas of struvite-based fertilizers that have not been studied yet, which could match specific crops and/or agricultural systems. However, current knowledge allows us to imply that struvite would be better used side by side with conventional water-soluble P sources if a maximum yield is the goal.

## Potential impacts for Brazilian crops

### Fruit trees

Studies on the use of struvite as a fertilizer for perennial fruit species are still lacking in the literature. A few studies involving perennial fruit trees and the use of struvite aimed at maintaining the mycorrhizal population when struvite was applied instead of a highly soluble phosphate fertilizer. In a study with apple trees, Van Geel et al. (2016) showed that the application of slow-release fertilizers enabled a greater diversity of arbuscular mycorrhizal fungi to cohabit the roots of apple trees compared to treatments with

high-solubility phosphate fertilizer. In some fruit-vegetable species, such as tomatoes, greater plant growth and nutrient absorption were observed with the application of struvite compared to high-solubility fertilizers (Di Tomassi et al., 2021). In addition to increasing the recycling flow of P from waste, the low solubility of struvite in water entails a lower risk of P loss, reducing potential environmental impacts (Everaert et al., 2018; Gu et al., 2020). Thus, the study of low-solubility phosphate sources is a gap in knowledge, especially for perennial crops, where the demand for P can differ between phenological stages.

In fruit trees, due to their perennial nature and woody structure, nutrients accumulate, leading to a greater nutritional demand throughout the physiological stages of growth. They also have a differential root distribution pattern and a preferential demand for some essential elements over others. It collectively makes them more nutritionally efficient than annual crops (Srivastava and Malhotra, 2017).

Like P, Mg is also present in the composition of struvite in considerable concentration (10 %). In orchard soils, Mg is either native or usually derived from applications of acidity correctors, especially limestone. However, limestone is applied before the seedlings are transplanted. When this happens, the limestone is applied to the soil surface and incorporated into the 0.00-0.20 or 0.00-0.30 m soil layers. When the need for application is diagnosed for producing orchards, limestone is applied to the soil surface (usually in small doses), which is not incorporated, to avoid physical damage to the root system. As a result, the descent of limestone particles or even their dissolution products, including Mg, into the soil profile is very slow (Kaminski et al., 2005; Olego et al., 2021).

Potential studies could be carried out on using struvite as a source of P in fruit species, especially when orchards are being planted, where soil correction and the application of doses of mineral P are normally carried out. With the slow release of P, it will be possible to verify the plants' responses during the first years of formation and estimate the relative P recovery by the plants. Fertilizing plants in the production phase, such as grapevines, has been shown to improve the nutritional status of plants. Phosphorus stimulates root growth, increasing the volume of soil to be explored, indirectly helping to absorb water and other nutrients, improving the nutritional status of the vines, and increasing productivity (Piccin et al., 2017). In soils with low P content, when supplemented with phosphate fertilizers, there is a visible increase in yield, such as in the number and weight of bunches and berries (Schmitt et al., 2020). This effect can be amplified with organo-mineral fertilizers, which can change the dynamics of P in the soil, favoring the absorption of P by plants at the stages of greatest need, such as the flowering season, for different fruit species.

**Table 2.** Characteristics of struvite as fertilizer in subtropical and tropical Brazil and recommended research actions

| Characteristics                                                                         | Research action                                                                                                    |
|-----------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| Variable crop responses                                                                 | More field experiments; No-tillage farming, Integrated Systems; and productivity assessment.                       |
| Poor supply of P in early plant growth, especially in the granulated form               | Calibration of fertilizing recommendations, especially using a mix of water-soluble P fertilizers and struvite.    |
| Low dissolution in soil of granulated form                                              | Granule formulas (e.g., struvite-based organo-mineral; blending); Interactions with solubilizing P microorganisms. |
| High residual effect                                                                    | Longer field experiments; intercropping cover-crops for improving P cycling                                        |
| Better fertilizer among the alternative P sources (e.g., animal manures, compost, Ca-P) | Calibration of co-fertilizing recommendation.                                                                      |
| Plants that exudate organic acids have higher P-struvite uptake                         | Plant breeding; intercropping cover-crops for improving P cycling.                                                 |
| Behavior in acidic Oxisols is virtually unknown                                         | Specific studies using P isotopes; Soil types; Levels of liming.                                                   |

In addition, root samples from three-year-old apple trees showed a higher arbuscular mycorrhizae (AM) diversity under struvite than inorganic fertilizers, and it was negatively correlated ( $r = -0.531$ ,  $p = 0.01$ ) to plant-available P in the soil (Van Geel et al., 2016). Despite that, this study did not evaluate plant growth. Arbuscular mycorrhizae are known to be affected by highly soluble P fertilizers, as diversity or roots' crop colonization sharply reduces and, consequently, benefits to plant nutrient uptake, especially P, are annulled. As a slow-release fertilizer, struvite would be expected not to have such a negative effect on AM.

### Grains

Some experiments can be cited to evaluate the performance of struvite as a source of P in grain production, such as canola (Ackerman et al., 2013), corn (Gell et al., 2011; Antonini et al., 2012; Uysal et al., 2014; Uysal and Kuru, 2015; Muys et al., 2021; Kokulan et al., 2024), beans (Arcas-Pilz et al., 2021), soybean and wheat (Omidire and Brye, 2022; Omidire et al., 2023). Although the efficiency of struvite in crops has been demonstrated, most of the studies were short-duration and in a protected environment, using pots with alkaline soils. Few studies have been carried out in the field, in long-term experiments, completing the plant life cycle, and accounting for grain production.

For instance, Omidire and Brye (2022) evaluated the use of struvite in the wheat-soybean production system for two years on a silt-loam soil (Aquic Fraglossudalfs) in eastern Arkansas, USA. They found that struvite did not differ from triple superphosphate in soybean and wheat, meaning it is a viable fertilizer option and a source of P and Mg for these crops. In another essay, also in Aquic Fraglossudalfs, Omidire et al. (2023) evaluated the performance of soybean [*Glycine max* (L.) Merr.] in two consecutive growing seasons in a P-deficient. Although the results with struvite were positive, both experiments were conducted in silt loam soil ( $750 \text{ g kg}^{-1}$ ), rich in calcium ( $1171 \text{ mg kg}^{-1}$ ) and magnesium ( $337 \text{ mg kg}^{-1}$ ). These conditions differ from those observed in the majority of grain cultivation areas located between the tropics, thus emphasizing the necessity of conducting field experiments with well-established protocols in these locations.

Struvite is commonly used as a source of low-water-soluble P. It has the potential to be used as a slow-release ammonium phosphate fertilizer, particularly when combined with highly water-soluble commercial P fertilizers like monoammonium phosphate (MAP). Experiments by Hertzberger et al. (2021) found that using up to 50 % struvite in similar biomass of corn resulted in a positive response. Similarly, using up to 25 % struvite in soybeans also yielded a positive response. The total P uptake by corn was the same across struvite mixtures ranging from 0 to 75 %, but significantly lower for 100 % struvite. The amount of residual P in the soil (Mehlich-3) decreased as more struvite was used to replace MAP. Based on the findings, it can be concluded that mixtures of struvite with MAP (25 to 50 % struvite) reduce the risk of P losses compared to MAP (Everaert et al., 2018), without limiting the initial (vegetative) growth of corn and soy. Other crops should be tested, as responses may vary in different crop species.

Another possibility is using struvite as a nitrogen fertilizer (mean concentration of 5.6 % N). Soto et al. (2023) evaluated two materials containing struvite powder from wastewater treatment as nitrogen fertilizers in agricultural soils with different pH values (8.2 and 6.7). Tests were held with incubation in soils without plants. These materials had a positive effect on soil fertility, especially in acidic soils, where struvite seems to be more soluble. It is believed that struvite will have similar efficiency to commercial nitrogen fertilizers in acidic soils, such as those in Brazil. However, associated with this process, an increase in soil salt content was observed (Soto et al., 2023), measured by high electrical conductivity (EC). Therefore, this parameter should be observed and monitored in the case of continuous applications of struvite, especially in conditions of poor drainage and/or low water regime, as it can be a limiting factor in crop development. These processes should be studied in detail in the future, considering that the N cycle in the soil significantly impacts soil chemistry and fertility and the soil microbiological community.

## Pastures

Since pastures need continuous nutrient management, struvite has emerged as a promising alternative to traditional fertilizers. Its production can be associated with managing manure from feedlots and dairy farms, using stabilization lagoons and biodigesters for its development. Struvite fertilizer is valued for its slow-release properties (Degryse et al., 2017), providing a steady supply of these nutrients to plants over time, especially in the acidic soils commonly found in pasture areas.

Magnesium content in struvite is equivalent to that found in dolomitic lime, while its P content is greater than that in single superphosphate, suggesting that using struvite in its more purified form effectively supplies both nutrients to pastures. Annual P removal through products like beef and milk ranges from 4 to 5 kg ha<sup>-1</sup> year<sup>-1</sup> (Urquiaga et al., 2023). Typically, P fertilization is carried out using single superphosphate, monoammonium phosphate, or triple superphosphate at rates of 10 to 50 kg ha<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub>, but can reach up to 200 kg ha<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub> for soils with low availability, particularly for highly demanding grass species (Monteiro, 2013). The main issue with acidic tropical soils is P fixation, a process that renders P unavailable by adsorption to soil colloids. For pastures adapted to tropical soils and managed extensively or with intermediate intensification, as it occurs in most pasture areas of Brazil, liming is recommended primarily to replenish Ca<sup>2+</sup> and Mg<sup>2+</sup>, rather than to reduce soil acidity, unless Al<sup>3+</sup> saturation is high (Monteiro, 2013). O'Donnell et al. (2021) demonstrated that struvite can effectively meet the P needs of pastures, enhancing root development and overall plant health while minimizing nutrient loss in non-acidic soils. Regarding N supply from struvite, additional supplementation may be required depending on the level of pasture intensification. In pastures supporting 1.1 to 2.2 animal units per hectare (A.U.= 450 kg live weight), N losses range from 34 to 57 kg ha<sup>-1</sup> year<sup>-1</sup> of N, primarily due to ammonia volatilization and the removal of animals for slaughter (Boddey et al., 2004; Homem et al., 2021). When N fertilization is employed, urea is commonly used as the N source, typically applied at rates of 100 to 150 kg ha<sup>-1</sup> year<sup>-1</sup> of N, not exceeding 50 to 70 kg ha<sup>-1</sup> of N per regrowth cycle to achieve optimal production response (Sales et al., 2020). Struvite can partially meet this demand, which could contribute to reduce environmental impacts, such as the greenhouse gas emissions associated with N fertilization (Wang et al., 2023b). In addition, N absorption by plants acidifies the soil, which may facilitate struvite dissolution, although the potential for soil acidification over time needs further assessment (Cabral et al., 2020). There is good potential for using struvite in grass pastures, which is even greater for mixed pastures with forage legumes. Legume species can meet a significant portion of their N demand through biological N<sub>2</sub> fixation, a process directly influenced by P availability (Bonilla and Bolaños, 2009). Pasture intensification based on mixed grass-legume systems allows for a certain extent of intensification (Homem et al., 2021), where fertilizer demands are low to moderate, which meets struvite's potential as a nutrient source. This approach contributes to the circular economy and promotes sustainable agricultural practices in livestock systems.

## Vegetables

Most vegetables can show a high P demand, often exceeding 100 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup>, which is higher than N and K demands. In general, P fertilization recommendations may vary, with levels reaching nearly 700 kg ha<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub> for tomatoes and 400 kg ha<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub> for carrots and cabbage in soils with low P content (Ribeiro et al., 1999; Freire et al., 2013; CQFS-RS/SC, 2016). The short growing cycle of vegetables leads to a high demand for prompt soluble P in the soil solution. Unlike N and K fertilization, which can be divided into two or three top dressings, total fertilization with P is carried out at the base, along with soil preparation, due to its low mobility in the soil profile. On the other hand, its residual effect can be advantageous because vegetables are planted sequentially in intensive cultivation.

Generally, vegetables are cultivated with organic fertilizers (poultry manure or compost) and conventional fertilizers (water-soluble sources) applied to the soil. This combination aims to supply nutrients over a longer period than the vegetable single cycle (residual effect) due to the slow release of nutrients from organic sources (Vieira et al., 2020) and to improve soil physics regarding porosity and water-holding capacity with the increase in soil organic carbon. In this sense, the slow-release property of struvite and its residual effect, especially for the granulated fertilizer form, might be an advantage in P supply in intensive vegetable cultivation. On the other hand, powder struvite, which has higher solubility in soil, could be feasible instead of its granulated form (Degryse et al., 2017), especially mixed with organic sources such as manure or compost.

Also, vegetables cultivated under no-till system and intercropping with cover-crops might have a positive interaction with struvite improving P use efficiency due to better soil exploration by the abundant root systems and the ability of some cover crops species to mobilize more P by exudation of organic acids and lower pH in the rhizosphere (Maltais-Landry, 2015; Alves et al., 2023).

Mycorrhizal tomato plants (35-day, greenhouse experiment, soil pH = 6.9) showed shoot biomass and P, N, and Mg uptakes significantly greater (Tukey's HSD test,  $p < 0.05$ ) when fertilized with struvite (granules) than with MAP (Di Tomassi et al., 2021). However, there was no difference in the apparent dissolution of struvite granules and the AM colonization of roots between struvite and MAP-fertilized tomato plants. Positive effect of struvite seemed to reside in promoting greater N uptake (or even Mg) with struvite fertilization.

Struvite application promotes an increase of other nutrients in the soil solution, such as Mg (Ahmed et al., 2018). Research on lettuce has demonstrated a significant increase in Mg absorption by plants, which is directly related to the higher Mg content in the composition of struvite (Cerrillo et al., 2015; Ryu and Lee, 2016). Magnesium supply is crucial in leafy crops due to its role in chlorophyll biosynthesis and particularly in crops that store plant biomass in bulbs and tubers - Mg is directly involved in carbohydrate synthesis (Grzebisz, 2013; Gerendás and Führs, 2013).

### Limitations and future perspectives

The potential of struvite-based fertilizers for Brazilian agriculture first faces the scale of production limitations. Although there is an array of agro-industrial and urban wastewater sources for struvite production, developing and implementing production units across the country may be slow and difficult, and depend on governmental incentives. On the other hand, struvite production is not a complex technology. It might have a relevant local and regional impact on nutrients from manure distribution as fertilizer and potentially add farm income, for instance, in Santa Catarina State and similar regions (Rocha et al., 2021). Finally, the higher cost of struvite than conventional soluble P-fertilizers would be a barrier to adoption (Rahman et al., 2014; Li et al., 2019a; Muhmood et al., 2019; Achilleos et al., 2022). In contrast, farmers' preference for solid fertilizer instead of slurries may be a drive in favor of struvite use. Below, we summarize some limitations and future perspectives for producing and using struvite-based fertilizers (Table 3).

**Table 3.** Limitations and future perspectives for struvite-based fertilizers in Brazilian agriculture

| Limitation                                                                                                                                               | Future perspective                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|----------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Scale of production.<br>Cost of production/fertilizer. Marketing.<br>To supply the crop early demand by P when due its slow dissolution when granulated. | Regional production associated with animal-confined operations and anaerobic digestion, such as swine production.<br>Production of struvite from sewage wastewater treatment plants.<br>Use of low-cost Mg sources (by-products, marine source) / Integration with wet oxidation technology.<br>Use of struvite alongside high soluble P-fertilizers to improve nutrient use efficiency.<br>Combine organic sources such as compost or animal manure with struvite to improve the fertilizer value of those organic sources. |

## CONCLUSION

Struvite production and use as slow-release fertilizer is a reality in many countries in North America and Europe. Its production comes mostly from municipal wastewater treatment plants and agro-industrial streams, resulting in decentralized production. In the literature, we found an array of review studies on struvite production and struvite use as a fertilizer. These studies show well-established knowledge on struvite precipitation processes and technologies and the vast majority of agronomic experiments were carried out in temperate and Mediterranean regions. There is a lack of studies on subtropical and tropical soils and climates, and none from Brazil have been found.

Considering struvite potential as a fertilizer, we highlighted that: (i) the crop response was quite variable, with a few field studies carried out so far; (ii) granulate and powder struvite have different fertilizing effectiveness (e.g., Degryse et al., 2017); (iii) soil pH will might affect more granulate struvite than powder struvite dissolution (e.g., Achat et al., 2014; Degryse et al., 2017); (iv) the slow dissolution of struvite, especially granulate, can result in a greater residual effect and lower losses of P (e.g., Rech et al., 2019); although no study had directly measured such effect; (v) a promising use of struvite seems to go along with soluble P fertilizers to sustain the highest crop yields (Talboys et al., 2016); (vi) struvite-based fertilizers have a higher efficiency as a P source than many alternative P sources such as manure, composts or phosphate powder rocks (Meyer et al., 2018); and, finally, (vii) very few studies were carried out in Oxisols (Everaert et al., 2017).

Therefore, the lack of studies in Brazilian soils is a barrier to precisely evaluating struvite as a fertilizer for Brazilian agricultural systems. The hypothesis that struvite would be a more efficient P fertilizer in Brazilian conditions still needs to be tested, especially for acidic Oxisols. The struvite effectiveness as a P fertilizer in Brazilian soils is still undetermined, especially those with high P fixation properties, and cropping systems such as no-till systems. The potentially higher residual effect of struvite on sequential crops than soluble fertilizers might be relevant in regions subject to heavy rains, sandy soils, and integrated systems (e.g., crop-forest; cover-crops). Brazil has a strong tradition in the research, production, and use of bio-products in agriculture, such as inoculants for BNF (e.g., soybean; common bean), P-solubilizing bacteria, and plant-growth-promoting rhizobacteria, which represents a link of synergy with struvite-based fertilizers. Again, research and experimentation are needed to come to a precise evaluation. Therefore, a consistent effort on struvite-based fertilizer agricultural experimentation in Brazil is necessary and would bring new insights for the sustainable use of P in tropical agriculture.

Finally, struvite production from swine wastewater can expand significantly in specific states in Brazil, where swine production is concentrated. Struvite production technology will be easily adopted and affordable for confined swine operations above 5,000 animals, which could yield about 300,000 Mg of struvite per year. The expansion of anaerobic digestion of swine manure can promote struvite production due to the release of P and the income from biogas and biomethane integrated into confined animal feeding units. On the other hand, although struvite technologies are widely used in developing countries, we should establish domestic technology to supply the potential demand.

## DATA AVAILABILITY

Not applicable. As a literature review, data are available in the original sources listed in the references.

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