University of São Paulo
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Phosphate sources derived from wastewater and sewage sludge: agronomic potential

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Dissertation presented to obtain the degree of Master in Science. Area: Soil and Plant Nutrition

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HEADING

> "The world is indeed full of peril, and in it there are many dark places; but still there is much that is fair, and though in all lands love is now mingled with grief, it grows perhaps the greater."
> *J. R. R. Tolkien*

SUMMARY

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RESUMO

Fontes de fosfato derivadas de águas residuárias e lodo de esgoto: potencial agronômico

O fósforo (P) é um elemento essencial para o metabolismo energético e produção de DNA/RNA nas plantas. No Brasil, elevadas quantidades de fertilizantes fosfatados são aplicadas anualmente nas áreas agrícolas para suprir a demanda das plantas, criando um cenário de risco económico, ambiental e de abastecimento. Para superar estas dificuldades, fontes fosfatadas recicladas de águas residuárias e lodo de esgoto surgem como uma alternativa aos fertilizantes convencionais, devido ao seu potencial de utilização agronômica e origens renováveis, reduzindo o impacto ambiental ao mesmo tempo que contribuem para a agricultura sustentável e uma economia circular. Estruvita e hazenita são minerais recuperados através da precipitação química das águas residuáriais, enquanto que o ashdec pode ser obtido através do tratamento termoquímico das cinzas de lodo de esgoto. Baixa solubilidade em água e liberação tardia, mais alinhada com a demanda das plantas, são características comuns destas fontes recicladas, que podem melhorar a eficiência da fertilização fosfatada. Neste trabalho, avaliamos a solubilização de estruvita, hazenita, ashdec e superfosfato triplo (TSP), suas dinâmicas de liberação de P e seus impactos no pH da solução e nas frações de P do solo através de um experimento de incubação em colunas de lixiviação. Também avaliamos seus potenciais e eficiências agronômicas em comparação com o TSP (fonte convencional escolhida), através de um ensaio em casa de vegetação durante dois ciclos de 90 dias de cana-de-açúcar (*Saccharum* spp.) sob essas fontes de fosfato em três doses de P (30, 60 e 90 mg kg^{-1}). Para cada colheita, foram analisados o rendimento de massa seca (DMY), parâmetros biométricos, absorção de nutrientes e frações de P do solo. Nossos resultados mostraram que embora as fontes recicladas sejam menos solúveis em água e promovam a liberação tardia de P, com menor solubilização de P comparadas ao TSP no período inicial, as plantas foram capazes de melhorar a utilização de P a partir destas fontes, uma vez que a estruvita (ambas as colheitas) e a hazenita (primeiro ciclo) tiveram um desempenho superior, enquanto o ashdec foi comparável ao TSP em DMY e absorção de P. Nos primeiros 90 d, todas as três fontes recicladas mostraram níveis de P lábil do solo mais elevados do que o TSP, única fonte que a aumentar a concentração de P não-labial ao final do experimento.

Palavras-chave: Reciclagem de fósforo, Águas residuárias, Lodo de esgoto, Estruvita, Liberação lenta, Potencial agronômico, Difusão de fósforo no solo

ABSTRACT

Phosphate sources derived from wastewater and sewage sludge: agronomic potential

Phosphorus (P) is a nutrient essential for energy metabolism and DNA/RNA production in plants. In Brazil, high amounts of P fertilizers are applied onto agricultural fields every year to supply plants demand, creating an economic, environmental and supply chain risk scenario. To overcome those issues, phosphate sources recycled from wastewaters and sewage sludge merge as an alternative to conventional fertilizers, due to their agronomic potential use and renewable origins, reducing environmental impact while contributing to sustainable agriculture and circular economy. Struvite and hazenite are minerals recovered via chemical precipitation from wastewaters, while ashdec can be obtained through thermochemical treatment of sewage sludge ashes. Low water-solubility and late release, more aligned with plants demand, are common characteristics of these recycled fertilizers, what could improve the efficiency of P fertilization. Here, we evaluated the solubilization of struvite, hazenite ashdec and triple superphosphate (TSP), their P release dynamics and their impact on the solution pH and on soil P fractions through an incubation leaching columns experiment. We also assessed their agronomic potential and efficiency compared to TSP (chosen conventional source) through a greenhouse trial for two 90 days cycles of sugarcane (*Saccharum* spp.) under those phosphate sources and three P doses (30, 60 and 90 mg kg^{-1}). Dry mass yield (DMY), biometric parameters, nutrient uptake and soil P fractions were analyzed for each harvest. Our findings showed that while the recycled sources are less water-soluble and promote late P release, solubilizing less P than TSP in the initial period, plants were able to improve P utilization from these sources, since struvite (both harvests) and hazenite (first cycle) outperformed, while ashdec was comparable to TSP in DMY and P uptake. In the first 90 d, all three recycled sources showed higher soil labile P levels than TSP, which was the only source increasing the non-labile pool by the end.

Keywords: Phosphorus recycling, Wastewater, Sewage sludge, Struvite, Slow-release, Agronomic potential, Soil phosphorus diffusion

1 INTRODUCTION

Phosphorus (P) is an essential element for plants, integrating cell membranes, DNA and RNA molecules and being crucial to energy metabolism (Butusov and Jernelöv, 2013). In most tropical soils, P is found in the soil solution in concentrations lower than 0.1 mg L^{-1} (Novais et al., 2007) and, due to the acidic and oxidic nature of these soils and their high P adsorption capacity, P uptake by plants can be significantly reduced (Roy et al., 2016), compromising crop productivity.

To supply plants' demand, P fertilizers are widely applied to agricultural systems, but conventional P sources are derived from phosphate rocks (PR), which are finite, non-renewable, and unevenly distributed in the globe, being considered a critical material (Cordell et al., 2009). The fertilizer industry is responsible for 90% of the consumption of all PR extracted worldwide (Pantano et al., 2016; Reetz Jr., 2016), and although literature diverges, it is generally agreed that this resource will eventually vanish, whilst depletion times of 50 - 100 years (Steen, 1998; Smil, 2000; Gunther, 2005), and 300 - 400 years (Van Kauwenbergh, 2010) have been suggested.

Also, the most used P sources are acidulated, highly water-soluble and their release dynamics are not aligned with plants demand, granting P fertilization a low efficiency (Lindsay 1979). As a way to improve P use efficiency and reduce the dependency on PR, P sources recycled from wastewaters and sewage sludge (SS) have been tested, and due to their lower water-solubility, they showed potential to reduce fertilizer-soil interactions and ultimately P fixation (Novais et al., 2007; Golroudbary et al., 2019).

Struvite ($MgNH_4PO_4.6H_2O$) and hazenite ($KNaMg_2(PO_4)_2.14H_2O$) are mineral fertilizers that can be obtained through chemical precipitation from wastewaters (Yang et al., 2011 & Yang et al., 2014), and merge as an alternative to the non-renewable sources of P. Besides being environmentally friendly, these sources are less soluble in water than conventional fertilizers (Watson et al., 2020), and can be more effective in agricultural systems, allowing greater plant uptake than highly-soluble sources (Cabeza et al., 2011; Weissengruber et al., 2018). Moreover, P recovery by sewage sludge ash (SSA) incineration is also possible via thermochemical processes where some alkaline compounds are degraded under high temperatures and react with phosphates creating bioavailable P compounds, while simultaneously evaporating toxic trace elements such as arsenic, cadmium and lead. After proper treatment of the SSAs, a low water-solubility P fertilizer ($CaNaPO_4$) is generated, which can be directly applied onto fields (Hermann & Schaaf, 2019).

The use of struvite, hazenite and ashdec as P sources can be beneficial for agriculture and the environment due to their recycled origin and solubility characteristics. This dissertation addresses their nutrient content and P solubility, their solubilization dynamics in the soil, P speciation, as well as their agronomical potential through incubation and greenhouse experiments in a Brazilian sandy clay loam Ferralsol, comparing them to triple superphosphate (TSP) in order to better understand these sources and their value for tropical agriculture.

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2 LITERATURE REVIEW

2.1 Phosphorus dynamics in soils

The comprehension of P dynamics and speciation in the soil is crucial to improve decision making on P fertilization for a more sustainable and productive agricultural system. In the soil, P is found mostly as orthophosphates ($H_2PO_4^-$ and HPO_4^{2-}) depending on pH. Those can be categorized as soil solution P and insoluble inorganic (Pi) or organic P (Po) (precipitated, adsorbed or as O.M. component) (Pavinato & Rosolem, 2008). On average, only 0.1% of the soil total P is available for plant uptake at a specific time, due to its low solubility (P concentration ranging from 0.001 mg L^{-1} and 1 mg L^{-1}) and its numerous interactions with the soil matrix, resulting in precipitation and/or fixation (Mahdi et al., 2012; Brady & Weil, 2013), highly dependent on soil pH.

In alkaline soils, P from fertilizer can be precipitated by calcium, and some sources such as superphosphate contain a high enough Ca concentration to precipitate half of its own P as dicalcium phosphate and/or its dihydrated form (Mahdi et al., 2012). In acidic soils, P can be fixed in clay minerals, especially by Al/Fe oxides and hydroxides, removing it from the soil solution and thus reducing its availability for plants (Parfitt, 1989; Luengo et al., 2006; Arai & Sparks, 2007). The fixation occurs through many reactions between soil and added P, such as precipitation, anion exchange, Al and Fe oxide surface reactions, formation of stable binuclear bridges among others.

Precipitation reactions are those in which hydroxyl phosphates are formed and, although initially somewhat soluble (due to high surface of exposure to the soil solution), its bonds age with time, decreasing its solubility and becoming sparingly available for plants. The anion exchange is when phosphates are adsorbed by kaolinite broken edges, an outer-sphere and reversible reaction. Oxide reactions are those where the phosphates substitute a hydroxyl group in the structure of an Al mineral. After that the phosphates may form stable binuclear bridges with the mineral surfaces, both these reactions are inner-sphere and highly difficult to break, making the P unavailable for crop uptake (Mahdi et al., 2012).

Tropical soils are usually highly weathered and acidic, which confers it a greater avidity for P adsorption when compared to temperate soils (Santos et al., 2018; Novais & Smyth, 1999). Apart from that, the natural low P concentrations in Brazilian soils (Du et al., 2020) and the viability of the P fertilizers use encouraged farmers to utilize it in large amounts in the last decades, increasing from virtually zero in the 1960s to 2.2 Tg yr^{-1} of P in 2016 (Reetz Jr., 2016; Withers et al., 2018).

2.2 Phosphate fertilizer efficiency

It is commonly accepted that P use efficiency of phosphate fertilization by crops is very low, between 10-25% (Lindsay, 1979) in the year of application, decreasing to 1-2% in the following years (Reetz Jr., 2016). However, recent field experiments have shown that this might not be the case (Johnston et al., 2014). A variety of studies have concluded that residual P can become available for crops in years after the fertilizer application, granting the practice higher efficiency than it was currently believed, sometimes exceeding 80% (Syers et al., 2008; Syers et al., 2010).

In that sense, efficient P fertilization management requires long-term strategies to increase its bioavailability and adequately supply plant demand (Shen et al., 2011), and good results have shown to reduce P fertilizer application by 20% for high-yielding cereal crops in North China, which could end up saving resources (Zhang et al., 2010). As previously discussed, P can present a multitude of chemical forms in the soil, all of which contribute to the plant-available P to a certain degree. The relative amount of available P found in a soil depends on a variety of factors within the system that alter P dynamics, such as soil chemical and physical properties, plant characteristics such as root development and adaptations, microorganism activity, environmental characteristics, fertilization or lack thereof (Walker & Syers, 1976; Cross & Schlesinger, 1995; Roberts & Johnston, 2015).

Generally, soil P forms can be group in three labilities (labile, moderately-labile and non-labile), each representing a certain level of adherence to the soil, and thus, of bioavailability. The P fractionation method proposed by Hedley et al. (1982) allows the sequential extraction of different phosphate forms, enhancing the comprehension of its soil dynamics and behavior. The labile P fraction comprises the P extracted by anion exchange resin (AER) and by sodium bicarbonate ($NaHCO_3$ 0.5 molar). While the AER extracts the soil solubilized Pi or weakly adsorbed Pi in oxy(hydroxides) and carbonates, the bicarbonate extracts the weakly adsorbed Pi and easily hydrolysable Po sorbed to the soil, and they are considered readily available for plant uptake (Mattingly, 1975; Cross & Schlesinger, 1995).

Historically, the application of phosphate fertilizers had as main goal to increase the soil labile P, allowing plants to match their requirements for healthy development and high productivity (Hinsinger, 2001; Vance, 2003). This is why highly water-soluble and acidulated fertilizers (such as TSP) were developed, aiming to be immediately available for plant uptake by quickly solubilizing in the soil solution. However, if these readily available phosphates are not rapidly absorbed by plants, they can lose their efficiency and gradually become less available with time due to soil-fertilizer interactions, especially in soils with high Fe/Al

oxi(hydroxides) content. This happens with fertilizer "aging" and the increase in the adsorption energy of the P bonds between these oxides, which ultimately ends up turning labile into moderately-labile and those into non-labile P if no contrary pressure is imposed upon the system, such as rhizosphere and microorganism's activity (Wang et al., 2013; Yoon et al., 2014).

The moderately-labile P fraction is represented by the P extracted by NaOH 0.1 molar and HCl 1.0 molar. Being adsorbed to the colloids with intermediate energy or bonded to other nutrients (such as Ca-P forms), this fraction can participate more actively in supplying phosphates to the labile fraction whenever the P in that compartment starts to be depleted due to plant uptake. This means that high concentrations of moderately-labile P in the soil could ultimately mean a high capacity of over time/late supply of P to plants under specific conditions (Guo & Yost, 1998; Gatiboni et al., 2007).

The non-labile P are the phosphates extracted by NaOH 0.5 molar, and the residual P (obtained after H_2SO_4 + H_2O_2 digestion), and are characterized as stable Po forms and recalcitrant Pi forms with very low solubility (Costa et al., 2016). In tropical soils, this P pool usually represents the highest values among all labilities, showing that a great amount of its total P is bonded to soil colloids with high energy, and thus are not immediately bioavailable.

To improve P uptake, plants are capable of adapting to scenarios of low P availability, since P starvation has been shown to induce changes to root structure, such as increasing the root/shoot ratio, root branching, elongation, and root hairs, besides an increase in topsoil exploration (Lynch & Brown, 2008). In some species of plants, P limitation might also cause the formation of cluster roots, structures that exudate organic acids chelating metal ions and mobilizing P and micronutrients as a result (Marschner, 1995).

Besides physical altering of structures, plants are equally able to induce chemical and biological changes in the rhizosphere, that can also increase P availability (Hinsinger, 2001). These changes, may involve the release of protons in order to acidify the rhizosphere, enhancing sparingly available P dissolution (Marschner 1995); besides the exudation of carboxylates, in order to chelate inorganic P and increase its absorption by plants (Neumann et al., 1999; Shen et al., 2005). Furthermore, plants are capable of secreting phosphatases, able to hydrolyze and mobilize organic P through enzyme reactions (Vance et al., 2003), which are dependent on P availability, soil pH, microorganism interaction, and physical and chemical characteristics of the environment (George et al., 2005).

Some soil and rhizosphere microorganisms can also enhance P acquisition by plants, either directly by solubilizing P, or indirectly by promoting plant growth through secretion of

hormones (known as phosphate solubilizing organisms – PSMs) (Richardson et al., 2009). The main mechanisms for PSMs are lowering the soil's pH (Tarafdar & Claasen, 1988), exudation of organic acids to dissolve once insoluble phosphates and to compete with P adsorption sites (Nahas, 1996).

Even considering the numerous and complex mechanisms by which plant and soil manage to solubilize P, it is still the most problematic nutrient in tropical agriculture. In order to improve nutrient usage, crop efficiency and sustainable production, it is necessary to integrate different disciplines, aiming to find solutions to current P management in agriculture (Shen et al., 2011). One alternative that is being explored is to re-use secondary P sources through recovery and recycling, such as livestock manures, crop residues and wastewater/SS, which, along with further investment in P recovery techniques, could potentially provide up to 20% of the crop P demand in Brazil, projected to be growing from 2.2 Tg yr^{-1} in 2016 to 4.6 Tg yr^{-1} in 2050 (Withers et al., 2018), thus substituting the current overuse of highly soluble inorganic fertilizers derived from phosphate rock (Withers et al., 2015).

2.3 Phosphorus recovery from wastewater and sewage sludge

World's population is continuously growing, from 7,7 billion people in 2019 to a projection of 8.5 billion by 2030 and 9.7 billion by 2050 (United Nations, 2019). Considering that urban areas are expected to absorb practically all of this future population (United Nations, 2018), there will be an increase in waste production worldwide, including SS. This scenario is also supposed to happening in Brazil, as shown by Kummer et al. (2016), also due to its inherent socio-economic development.

The increase in the implementation of sewage collection and treatment processes in Brazil is creating a growing volume of wastewater and SS residues, which are chemical/physically complex and demand solutions that usually go beyond the wastewater treatment plants (WWTPs). The negligence in giving this material a proper treatment resulted in a series of environmental issues that only started to be addressed in the last decade (Andreoli & Pegorini, 2006). What is clear is that the demand for improving these processes is urgent, being now pushed by the new Legal Framework for Basic Sanitation (https://www.gov.br/pt-br/noticias/transito-e-transportes/2020/07/novo-marco-de-saneamento-e-sancionado-e-garante-avancos-para-o-pais), to be implemented until 2033.

The SS is produced in WWTPs, when suspended solids are removed from the wastewater, while organic substances are assimilated into bacterial biomass, that will be part of the sludge composition (European Environmental Agency, 1997). According to the

Brazilian National Sanitation Information System (SNIS, 2020) only 49.1% of the wastewaters produced in the country were treated in 2019, whilst disposing approximately 5.129.167m³ of untreated wastewater in waterbodies (Instituto Trata Brasil, 2019). This shows there is still plenty of room for growth and development in wastewater collection and treatment, and of the residue that is currently being generated only 15% was used in agriculture in the year 2008 (Machado, 2008).

According to Nogueira et al. (2008), SS is very rich in organic matter and other elements of interest, and could play a vital role in agriculture by substituting some of the mineral fertilizers that are currently used, ultimately leading to a decrease in fertilization costs (Kummer et al., 2016). Although the data on waste production worldwide is deficient, it is still relevant that nutrients such as nitrogen and P present in these materials are recovered, for it could bring economic, social and environmental benefits (Mateo-Sagasta et al., 2015). Studies in Brazil have shown the benefits of using SS as a substitute for conventional fertilizers, helping to recover degraded areas (Teixeira & Melo, 2007). However, its direct application on agricultural areas is considered controversial, because SS often contain hazardous substances like organic pollutants, heavy metals and pathogens (Havukainen et al., 2016, Vogel et al., 2013).

As a way to reduce the impact of these pollutants and increase P recovery and bioavailability, different techniques are being explored, such as chemical extraction of P from the SS by struvite precipitation (Melia et al., 2017). Struvite ($MgNH_4PO_4{\cdot}6H_2O$) is a phosphate mineral that naturally precipitates in wastewater treatment plants (Cordell et al., 2011), attending a double interest, the production of a potentially efficient recovered P fertilizer (Le Corre et al., 2009) and the removal of P from the water that will return to the environment, reducing and preventing eutrophication of surface waters (Cordell et al., 2011).

Struvite precipitation from wastewater can achieve P recovery rates higher than 90% (Xavier et al., 2014, Shokouhi, 2017), although Krüger & Adam (2017) mention that this parameter, along with the P bioavailability, is dependent on the content and species of P that are present in the treated SS. As P associated with Mg/Ca hydroxides are more phytoavailable than those associated with Fe/Al, many studies have been conducted aiming to enhance their viability by struvite precipitation (Vogel & Adam, 2011). Degryse et al. (2017), for instance, concluded that struvite granules precipitated by using $MgCl_2$ and MgO in the correct proportions performed better when compared to those formed with an excess of MgO, because in this scenario, the remaining bases captured could increase soil's pH around the granule, decreasing struvite dissolution.

Although struvite precipitation has received the most attention among all the wastewater P recovery methods for its utilization as a fertilizer (Weeks Jr. & Hettiarachchi, 2019), its efficiency has to undergo more research and testing in order to be confirmed, especially in tropical conditions. Its performance has been reported to differ according to factors such as application method, granulometry and soil pH (Degryse et al., 2017, Le Corre et al., 2009, Everaert et al., 2017; Talboys et al., 2016).

Otherwise, the incineration of SS into SSA is another way to concentrate nutrients and eliminate some pollutants that might be contained in the raw material. This procedure is usually done at 850-900 ºC, temperature under which, according to Shaikh (2018), P takes the form of volatile oxides, that upon cooling will condense to P_4O_{10}, as a component of the SSA. The P concentrations on SSA averaging 15% (as P_2O_5) have been obtained, indicating that it could be a good alternative to produce P-fertilizers (Cyr et al., 2007, Donatello et al., 2010).

After the SSA obtainment, it can be treated upon addition of salts of Ca or Mg, aiming to increase P availability by converting its $Ca_3(PO_4)_2$ to more bioavailable forms, through thermochemical treatment (Adam et al., 2009). Methods that could be used for recovering P from SSA would be sorting or leaching processes, the first being usually preferred for it requires less technology and can be done with considerably lower consumption of chemicals when compared to leaching (Franz, 2007).

Across the globe there are over 80 identified struvite-producing plants, although data on Asian structures are still scarce. These installations operate through 19 different technologies (Kabbe et al., 2019). Currently, Europe stands as the region with the greatest number of full-scale installations producing struvite, in which the main contributing countries are Germany (10), The Netherlands (10), Belgium (6), Denmark (4) among others, for a total of 37 plants (Shaddel et al., 2019; Kabbe et al., 2017; Oleszkiewicz et al., 2015).

In Europe, it is estimated that 15,000 tons of the fertilizer is produced each year (Huygens et al., 2019). Municipal wastewater is the main primary source for this production, although other materials such as industrial wastewater and manure are also used (Kabbe et al., 2017; Elhert et al., 2016).

Although North America does not have as many struvite recovering plants (with 15 active sites) when compare do Europe, its volume of precipitated struvite is higher, and although data is deficient, it is estimated that its production stands well above 17,500 tons of struvite per year (Kabbe et al., 2015; Walker, 2017; Kabbe, et al. 2017). China and Japan are also responsible for a substantial amount of struvite production (Kabbe et al., 2017).

Kok et al. (2015) estimated the potential total amount of P recoverable from human and livestock residues per continent (Table 1). This estimation, however, does not take into consideration the economic viability of the process. When analyzing a model that considered phosphorus quantities, prices and distances between production plants, the authors estimated that, in a market where rock-based fertilizer is present, only 0.15 Mt year^{-1} of P could be economically recovered, thus satisfying only 0.8% of the global agricultural demand. However, in a scenario where rock-based fertilizers are scarce or non-existent, 7.92 Mt could be economically recovered, representing 41% of the total agricultural demand.

Table 1. Approximate continental potentially recoverable P from human and livestock residue.

Continent	Livestock production	Human production (Mt P)	Agricultural demand
Asia	5.85	2.29	9.49
North America	3.10	0.31	3.30
Europe	2.39	0.40	1.79
Africa	1.72	0.53	2.51
South America	3.89	0.22	2.17
Oceania	0.32	0.01	0.24
World	17.11	3.75	19.52

For being environmentally friendly and having low water solubility and slow diffusion characteristics, struvite and SSA derivates are believed to be outstanding P fertilizers, capable of better supplying the crops demands than soluble sources. Further studies have to be conducted in order to fully understand the potential and characteristics of this products as fertilizers for crops, especially in tropical conditions.

2.4 Struvite and SSA efficiency

The most commonly used sources of P in agriculture are the highly water-soluble phosphates, such as monoammonium (MAP), diammonium phosphate (DAP); triple and single superphosphate (TSP and SSP) (IPNI, 2010). All of these fertilizers are highly soluble in water and present fast P release, being rapidly available for plant uptake (Robertson et al., 2012). For this, they tend to suffer from quick fixation, especially in acidic soils, with high clay and Fe/Al oxi(hydroxides) content.

According to Noor et al. (2017), the use efficiency of P from fertilizers applied to agricultural systems is very low, not exceeding 25% under all circumstances, becoming an issue to almost all soils. The authors also point out that the current phosphate fertilizers

commercially available are not being able to successfully supply plants demand for a sustainable crop production. To achieve higher yields, some techniques are being explored, aiming to reduce fertilizer P adsorption by the soil and thus increasing uptake by plants. One possibility to improve P use efficiency is by coating fertilizers with suitable materials to reduce P solubilization speed in the soil, that could increase crops productivity, even if by small rates (Trenkel, 2010). However, coating should be effective and economically viable, although currently most available polymers tend to be expensive, increasing the production cost (Noor et al., 2017).

Following the trend of low solubility sources, some studies have focused on evaluating the effectiveness of struvite, but few scenarios were explored, and thus conclusions are still open for debate. According to Shokouhi (2017), struvite usually consists of 13% P, 6% N and 10% Mg, and could be used as a slow-release fertilizer. It is expected to have a P-release dynamic more aligned with plant uptake, increasing P efficiency, enhancing the absorption by plants while decreasing the fixation of P in soil's colloids (Heppell et al., 2015).

For now, most pot trials using struvite granules failed to produce the same aboveground biomass as the MAP treatments, irrespective of conditions, although Degryse et al. (2017) concluded that, under acidic soils, ground struvite produced plant biomass comparable to MAP, indicating that particle size could increase the efficiency of the product. This evidence suggests that, while struvite could be an efficient late release fertilizer, its short-term efficiency is compromised by its low solubility in water. Therefore, Talboys (2016) conducted a study blending struvite and DAP (20/80 proportion), in the intention of stimulating early and late-season release, and observed that early P uptake matched 100% DAP, and that this blend could ultimately reduce struvite dissolution, due to high P concentrations in the collocated granules.

Moreover, Everaert et al. (2017) observed that even though struvite showed lesser diffusion in the soils tested (acid, neutral and calcareous), < 8mm from the point of application when compared to MAP, it presented greater lability, probably because the struvite granules had not completely dissolved. Further studies must be conducted in different scenarios for a better understanding of struvite's efficiency versus soluble fertilizers, such dosages, forms of application, crops, soil and struvite characteristics like solubility, nutrient content, solubilization, granulometry and so on, to come with a definitive conclusion.

Besides struvite, the use of SSA as fertilizer may become a viable way to dispose the SS from wastewater treatments, supplying P and other nutrients in agriculture. The interest in the SSA as a P source came from the its high production by some European countries, such as

Germany, the Netherlands, Switzerland and Austria, where SS incineration is widespread. In Germany, for instance, a survey showed that 19000 t of P are being recycled each year through SSA. However, the bioavailability and agronomic efficiency of the nutrient contained in this material is low. For this reason, thermochemical treatments are being developed in order to transform the ashes into more efficient fertilizers, such as the ashdec. Additionally, toxic elements such as arsenic, cadmium, mercury, lead etc. are also removed from the final product, fulfilling the requirements for a P-fertilizer (Herzel et al., 2016).

In a pot experiment, Nanzer et al. (2014) tested two types of SSAs (SSACa and SSAMg) and observed that SSAMg performed comparably to KH_2PO_4 (water-soluble) in terms of P recovery by ryegrass and soil bioavailable P pools after incubation. Furthermore, the effectiveness of both SSAs relative to KH_2PO_4 was greater in acidic and in low P concentration soils when compared to more alkaline ones or with higher available P. In another study, Kratz et al. (2017) tested five different SSA fertilizers compared to SSP and control, obtaining only small and, in most cases, non-significant differences in wheat's dry matter yield with SSAs amendments compared to SSP and control, while P uptake was significantly higher in all treatments when compared to the control, concluding that the availability of the SSA derived fertilizers has to be further enhanced and analyzed.

Due to the diversity of agricultural systems, crops and conditions, studies and research on recycled P sources, especially in tropical soils, are important to understand their characteristics, behavior and agronomic potential, and could possibly merge as outstanding alternatives to conventional sources for Brazilian sugarcane production.

2.5 Hypothesis

Struvite, hazenite and ashdec, as P sources recycled from sewage sludge and wastewaters, are environment-friendly and more efficient phosphate fertilizers, reducing P adsorption in tropical agricultural soils and supplying crop P requirements more effectively when compared to conventional sources.

2.6 Objectives

General:

Characterize three recycled P sources (struvite, hazenite and ashdec) and evaluate their agronomic potential in supplying sugarcane P demand in the short-term compared to triple superphosphate (TSP).

Specific:

Characterize two types of struvites (struvite and hazenite) and an SSA based fertilizer (ashdec), describing their nutrient content, P solubility, release dynamics, effect on soil solution pH and P speciation in the soil through a leaching columns incubation experiment;

Evaluate the agronomic efficiency and residual effect of both struvites and the SSA based fertilizer in two 90 days cycles of sugarcane, assessing their potential in P supply and speciation in a sandy clay loam Ferralsol in a greenhouse experiment compared to TSP.

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3 PHOSPHORUS SOLUBILITY AND DYNAMICS IN THE SOIL UNDER SOURCES DERIVED FROM WASTEWATER AND SEWAGE SLUDGE

Abstract

Conventional phosphate fertilizers are usually highly water-soluble and are rapidly solubilized when in contact with the soil solution. However, if this solubilization is not in alignment with plants demand, it can react with the soil colloidal phase, becoming less available overtime, especially in acidic, oxidic tropical soils, with high adsorption capacity, reducing the efficiency of P fertilization. Furthermore, these fertilizers are derived from phosphate rock, a non-renewable material, generating an environmental impact. To assess these concerns, P sources recycled from wastewaters (struvite and hazenite) and sewage sludge (ashdec) were studied for their potential of reducing P fixation by the soil, improving the agronomic efficiency of the P fertilization. In our work, we compared the solubilization dynamics of struvite, hazenite, ashdec and TSP in a sandy clay loam Ferralsol, as well as their effect on solution pH and on soil P pools (labile, moderately-labile and non-labile) via an incubation experiment. Leaching columns containing soil with surface application of 100 mg col^{-1} of P from each selected fertilizer and one control (nil-P) were evaluated for 60 days. Daily solution samples were analyzed for P content and pH. Soil was stratified in the end and submitted to P fractionation. Our findings showed that TSP and struvite promoted an acid P release reaction, while ashdec and hazenite reacted alkaline. Furthermore, TSP promoted a rapid yet not sustained release of P throughout the trial while hazenite and struvite showed late release dynamics. Otherwise ashdec solubilized no P over the period analyzed. All recycled sources promoted higher soil labile P concentration than TSP, and ashdec showed high moderately-labile P, reaffirming its late release potential.

Keywords: Phosphate dynamics, Phosphate diffusion, Struvite, Wastewater, Sewage sludge, Phosphate leaching, P speciation.

3.1 Introduction

Organic and inorganic forms of phosphorus (P) are usually found in soils irrespective of natural or cultivated condition. Those forms are partially available in solution, but mostly retained in the clay minerals with different energy levels that vary from adsorbed to the crystalline structure of some minerals to stable organic fractions (Gatiboni et al., 2007). Most Brazilian soils are intensively weathered, prone to electropositivity and, ultimately, to high P fixation (Baldotto & Velloso, 2014).

To meet crops needs, phosphate fertilizers are widely used in agricultural systems. Conventional sources are acidified, totally soluble in water and will deliver P to the soil solution as soon as the granule is moistened. However, due to phosphate-specific adsorption mechanisms, aggravated by the tropical soils' characteristics, P recovery by plants is usually low, granting phosphate fertilization a very low efficiency (Guedes et al., 2016), not exceeding 25% in most cases (Noor et al., 2017).

One way to increase this efficiency is by developing less water-soluble fertilizers, with a more synchronized P solubilization according to crop demand, that can be classified as slow-release, defined by Trenkel (1997) as those containing a nutrient in a form in which its availability is either delayed or is available for plant uptake for longer than a reference fertilizer, in this case, the "rapidly available" acidulated phosphates such as triple

superphosphate (TSP) or monoammonium phosphate (MAP). By increasing the interval in which a fertilizer is able to supply P for the soil solution, adsorption decreases and P uptake by plants can potentially be increased, resulting in healthier and more productive crops (McLaughlin et al., 2011), along with many beneficial side-effects to the whole agricultural system such as enhanced root growth, micro-organisms stimuli, nutrient recycling, etc. (Syers; Johnston & Curtin, 2008).

Struvite ($MgNH_4PO_4·6H_2O$) is a mineral fertilizer obtained through chemical precipitation from wastewaters/sewage sludge (SS), and merges as an alternative to the non-renewable sources of P used in the current conjecture for agriculture. Besides being environmentally friendly, struvite is less soluble in water than conventional fertilizers. Therefore, it can be more effective in agricultural systems, with gradual solubility in the soil solution, allowing greater plant uptake than highly-soluble sources (Cabeza et al., 2011).

Hazenite ($KNaMg_2(PO_4)_2·14H_2O$) is an alkaline struvite-type phosphate mineral recognized as such at the beginning of 2008 (Yang et al., 2011 & Yang et al., 2014). It can also be precipitated from nutrient rich wastewaters, and like struvite, presents low water-solubility (Watson et al., 2020). Literature regarding its performance as a P fertilizer is still scarce, but it has shown potential as a slow-release fertilizer with good P-effectiveness (Weissengruber et al., 2018).

Moreover, another way to treat SS and recover P is by incineration in a thermochemical process, where some alkaline compounds are degraded under high temperatures and react with phosphates creating bioavailable P compounds, while simultaneously evaporating toxic trace elements such as arsenic, cadmium and lead. After specific treatment of the sewage sludge ashes (SSA), ashdec (basic composition $CaNaPO_4$) is generated, a concentrated and citrate-soluble P fertilizer that can be directly applied onto fields (Hermann & Schaaf, 2019).

Due to the differences in solubility and soil dynamics between conventional phosphate fertilizers and these sources recycled from wastewater treatment plants (WWTPs), they may be more efficient for crop supply over the growth cycle. Our objectives were to characterize the nutrient content and P solubilization dynamics, to evaluate soil P transformations, as well as the effect on the solution pH caused by three phosphate fertilizers recycled from wastewaters and sewage sludge: struvite, hazenite and ashdec, comparing them to triple superphosphate ($Ca(H_2PO_4)_2$), the most commonly used mineral phosphate fertilizer.

3.2 Materials and methods

The research was developed at the College of Agriculture Luiz de Queiroz – ESALQ/USP, studying the conventional phosphate fertilizer (TSP) compared to three distinct sources recycled from German WWTPs , in partnership with the German Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und -prüfung - BAM), the Berlin Centre of Competence for Water (Komptenzzentrum Wasser Berlin - KWB), and Outotec GmbH & Co.KG, a private company that works on recycling P from wastewaters and sewage sludge. The tested sources were struvite and hazenite, both precipitated from wastewaters (supplied by KWB), and AshDec®, a fertilizer co-developed by BAM and Outotec, from the thermochemical treatment of SSA.

3.2.1 Experimental Setup

The fertilizers solubility evaluation was done through leaching in acrylic columns, kept under indoor incubation. The soil used in the experiment was collected from the surface layer (0-20 cm) of a grassland area, and described as a sandy clay loam Ferralsol (FAO, 2014), with very low P availability according to the criteria described by Raij et al., (1997). The soil was air-dried and sieved using a 2 mm mesh sieve. Its chemical and textural characterization is shown in Table 1.

Table 1. Soil chemical and textural parameters before experimental setup.

pH CaCl$_2$	O.M.	P	S	K$^+$	Ca^{2+}	Mg^{2+}	Al^{3+}	H + Al	SB	CEC	V	m
-	g kg^{-1}	mg kg^{-1}		--------------------mmol$_c$ kg^{-1}--------------------							%	
4.9	16	5	6	<0.9	13	5	12	16	18.8	34.8	54	10
				Clay	Silt	Sand						
				---------g kg^{-1}---------								
				201	11	788						

O.M = Organic matter; SB = sum of bases; CEC = Cation exchange capacity; V = base saturation; m = Al saturation.

Overall, the soil fertility levels were very low / low for all macronutrients, also presenting low O.M. levels, small CEC and considerably high Al saturation (m%). No pH correction was done to the soil prior to the trial, for the addition of Ca could ultimately lead to a change in behavior of the phosphate fertilizers, that could end up increasing the formation of calcium-phosphates. No other nutrient was added to the soil except P and those contained in the treatment sources.

For water retention, the soil's maximum water holding capacity (MWHC) was determined according to the ISO (2003) method, with minor adjustments. In short, 120g of dried soil were transferred to plastic cups with holes on the bottom, sealed by a nylon membrane (0.075 mm mesh), and placed on a water saturated bed of sand for 24 hours, enough time for the water to flow upwards by capillarity, filling the soil's pores until saturation. The MWHC was calculated as the difference between dry and saturated soil weight. This data was used in order to maintain soil saturation throughout the whole experiment duration.

For the column's settlement, thermoplastic acrylic tubes of 2.1 cm in internal diameter and 25 cm long were used. A nylon lid was coupled on the bottom of the tubes with a hole poked in the middle, where a plastic hose was attached in order to collect the percolated water. The columns were then placed in a wooden support and 50 g of dry and sieved soil were added to each one. Following, distilled water was added to achieve MWHC. Treatments consisted of four distinct P sources (struvite, hazenite, ashdec, triple superphosphate) and a control (nil-P) with four replicates, in a completely random design. The chemical characterization of the sources is presented on Table 2. Once the columns were saturated with water, the corresponding fertilizers for each treatment were added on the topsoil in the dose of 100 mg of P per column.

Table 2. Nutrient content of fertilizers sources used as treatments.

Fertilizers	K	Ca	Mg	Na	P_2O_5 total	P_2O_5 water	P_2O_5 HCi
					%		
Struvite	-	-	8.3	-	28.7	1.56	28.4
Ashdec	0.8	9.5	1.5	11	16.6	0.72	15.6
Hazenite	7.1	-	7.3	-	24.7	3.32	24.3
Triple Superphosphate	-	10	-	-	45.0	40.5	45.0

*water = water soluble; HCi = soluble on citric acid 2%.

3.2.2 Sampling procedure and measurements

Under each column, 70 mL caps were placed aiming to retain the leached solution. Above each support, a saline kit was fixated, containing 300 mL flasks, adapted to enable periodical water dripping with controlled flow rate over the columns.

Once the fertilizers were applied, 10 mL of distilled water were added every single day for 30 days, and then every second day for 30 more days. The average amount of solution collected per application was 8.4 mL per column. The leached solution was collected and

measured for its P content through the blue-molybdate methodology described by Murphey & Riley (1962), and solution's pH was determined by an electronic pHmeter.

After 60 days, the columns were disassembled and the soil was sampled in the layers of 0-1, 1-2, 2-4, 4-6, 6-8 and 8-10 cm from the top, and dried at 40ºC. Soil samples were submitted to P fractionation by procedure described by Hedley et al. (1982), modified by Rheinheimer (2000), briefly described as follows: Samples of 0.5 g are submitted to the sequential extractors in the following order: anion exchange resin (readily plant-available fraction), $NaHCO_3$ 0.5 mol L^{-1} (organic and inorganic labile fractions), NaOH 0.1 mol L^{-1} and HCl 1.0 mol L^{-1} (moderately-labile organic and inorganic fractions) and NaOH 0.5 mol L^{-1} (organic and inorganic non-labile fractions). All extractions were done after 16 hours shaking in 10 mL extract, using an end-over-end shaker at 33 rpm. After the extractions, 0.1 g of samples' residues were submitted to a H_2SO_4 + H_2O_2 digestion to determine residual P. The Pi content in the extracts was quantified by colorimetry (Murphy & Riley, 1962), and the Po in the $NaHCO_3$, NaOH 0.1 mol L^{-1} and NaOH 0.5mol L^{-1} was calculated as the difference between total P and Pi.

The data was grouped for each treatment in: daily accumulated P leached in solution and daily pH; soil labile, moderately-labile and non-labile P (for each depth) at the end of incubation time. Labile P are the phosphates that are either in or in osmotic equilibrium with the soil solution, and thus can be easily accessed by plants. The moderately-labile fraction is represented by the phosphates that are adsorbed with an intermediate energy level, such as dicalcium phosphates, and that could possibly supply plant demand in a medium/long period of time, by releasing it to the labile fraction. The non-labile P fraction is non plant available and will not become so in the short to medium term. Phosphates in this compartment are either adsorbed to the colloids with high energy or are inside its crystalline structure, having to undergo weathering in a geological time scale in order to possibly be released from its bonds (Yang & Post, 2011).

The P recovery (%) for the experiment was calculated as follows (I), by assuming that the total P in the control treatment plus 100 mg col^{-1} of P added via fertilizer corresponded to 100%.

I.   P recovery (%) = (P_{soil} + P_{sol})/ (P_{ctrl} + P_{fert})

In which P_{soil} equals the total P recovered from fractionation, P_{sol} is the P leached in the solution; P_{ctrl} is the sum of soil and leached P in the control and P_{fert} is the P added via

fertilizers. The P recovery varied from 96 - 98%, similar to results reported by Zhang et al., (2020). Detailed data can be found in the supplementary Table S1.

3.2.3   Statistical Analysis

All data were subjected to the normality test (Shapiro-Wilk) and posteriorly to analysis of variance (one way ANOVA). Means were compared through Tukey test. A t-test (LSD) was done to compare daily solubilized P. All analysis were conducted in the R statistical software considering $p < 0.05$.

3.3 Results and discussion

3.3.1   Solution pH

By monitoring the solution pH, it was possible to see that the control treatment maintained similar pH level (7.12 ± 0.33) throughout the whole incubation time. Meanwhile, fertilizers changed the solution pH considerably. Struvite and TSP promoted a decrease in solution pH as the sources solubilized in the soil, inferring the occurrence of an acid reaction (Figure 1). TSP promoted a rapid yet not-sustained decrease in pH, going from an average 6.68 on day zero to a 4.38 on day one, increasing gradually afterwards, returning to the initial value by 23rd day, at which point the pH was maintained on the same level throughout the experiment.
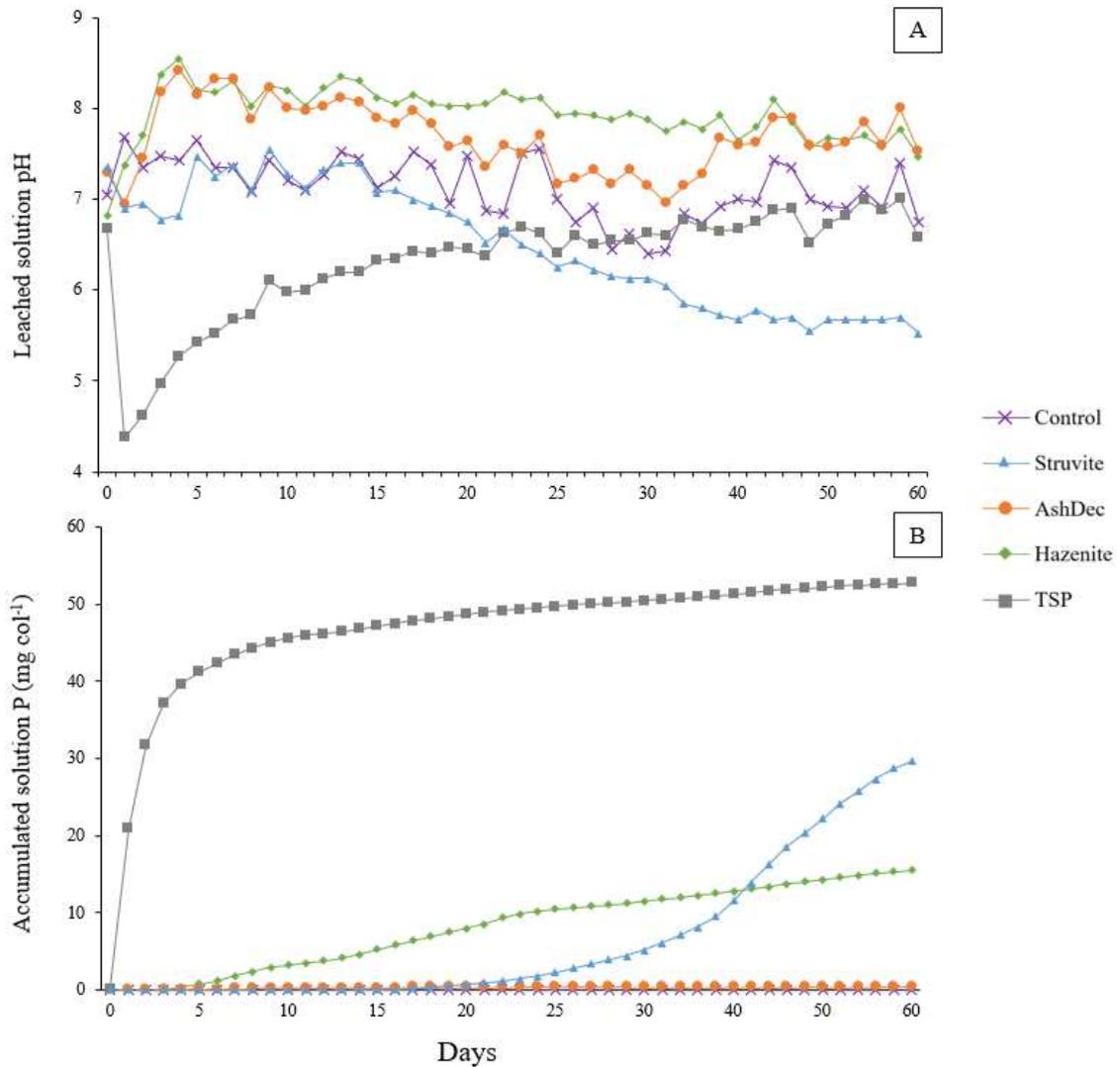
Figure 1. Daily pH means (A) and daily accumulated solubilized P (mg col^{-1}) (B) under distinct phosphate sources.

This pH change may be explained by the release of H^+ by the initial dissolution of the TSP granules (FTRC, 2015). Two subsequential reactions take place, the first generates acidity, and the second one neutralizes it by releasing a hydroxyl, as seen below:

II. $Ca(H_2PO_4)_2 + H_2O \rightarrow CaHPO_4 + H^+ + H_2PO_4^-$

III. $CaHPO_4 + H_2O \rightarrow Ca^{2+} + H_2PO_4^- + OH^-$
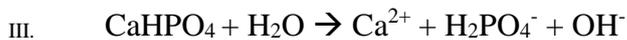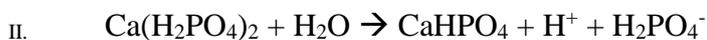
Due to its high water-solubility, most of the phosphates are quickly dissolved according to the first reaction described, which ends up acidifying the solution momentaneously. However, after most of the $Ca(H_2PO_4)_2$ dissolution to $CaHPO_4$, reaction III becomes more relevant, thus neutralizing the acidity generated by reaction II, justifying the behavior of the pH (Lindsay, 1979; Fernández et al., 1999).

Struvite, on the other hand, maintained the pH relatively stable (7.35 – 7.10) from the beginning of the dissolution until day 15th, when it begins to decrease until reaching its

minimum value (5.53) at the last day of evaluation (day 60) (Figure 1A). According to Kecskésová et al. (2020), struvite precipitation requires specific conditions, such as alkaline pH, and changing these conditions reduces crystallization, allowing dissolution. Due to the fairly acidic soil pH (pH_{CaCl2} = 4.9) used here, struvite solubilization was induced to a certain extent. According to Doyle & Parsons (2002), struvite's dissolution obeys the following reaction:

IV. $MgNH_4PO_4 \cdot 6\,H_2O \rightarrow Mg^{2+} + NH_4^+ + PO_4^{3-} + 6\,H_2O$
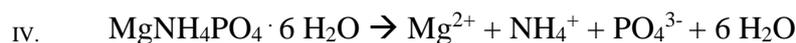
The solution acidification observed (Figure 1A) can be attributed to struvite's release of ammonium to the solution, that can suffer autotrophic microbial nitrification, which produces H^+ according to reaction V (Tarre & Green, 2004).

V. $NH_4^+ + 1.5\,O_2 \rightarrow NO_2^- + 2H^+ + H_2O$
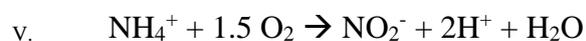
Although it is generally accepted that the growth of autotrophic ammonia oxidizing bacteria (AOB) in liquid culture do not happen in pH values below 6.5 (Painter, 1986; Burton & Prosser, 2001), many authors have reported low rates of nitrification and the presence of nitrifying bacteria in acidic soil conditions, even in pH as low as 3.3 (Hayatsu & Kosuge, 1993; De Boer & Kowalchuk, 2001; Burton & Prosser, 2001). Moreover, De Boer & Kowalchuck (2001) indicated that some acid-tolerant AOB (*Nitrospira* spp.) could be active in low pH values even without NH_3-generating mechanisms. Yet, the authors point out that some microsites of alkaline pH might allow nitrification, what may have occurred in our data due to the fairly high initial solution pH found in the struvite treatment.

Ashdec and hazenite, in turn, increased the solution's pH compared to control, while never returning to the starting point. In despite of the low amounts of P solubilized by the ashdec treatment, we hypothesize that the following reaction (VI), suggested by Messerschmitt (1938), may generate sodium carbonate that further reacts according to reactions (VII and VIII), and could explain the pH increase associated to the extremely high dose and water volume applied to the columns, when even small amounts of solubilized fertilizer could have been sufficient to generate enough hydroxyl to change the solution pH.

VI. $2\,CaNaPO_4 + CaSiO_3 + CO_2 \rightarrow Ca_3(PO_4)_2 + Na_2CO_3 + SiO_2$

VII. $Na_2CO_3 + H_2O \rightarrow 2\,Na^+ + HCO_3^- + OH^-$

VIII. $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$
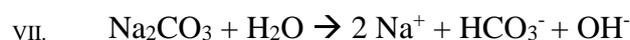
Hazenite's dissolution reaction (IX) can be seen below (Yee, 2018).

IX. $KNaMg_2(PO_4)_2 \cdot 14H_2O \rightarrow 2\,Mg^{2+} + K^+ + Na^+ + 2PO_4^{3-} + 14\,H_2O$

Another interesting aspect is that phosphate fertilizers solubilization may increase under low pH, such as those where plant roots are excreting organic acids, contributing to the availability of phosphates in the rhizosphere. Liu et al. (2016) found that, in a naturally acidic soil (pH = 5.3), struvite along with acid irrigation water (pH = 6.0) resulted in higher aboveground mass and P uptake by bird rapeseed (*Brassica campestris* L.) when compared to the same struvite and to a calcium phosphate fertilizer both irrigated with neutral water (pH = 7.5).

Other results corroborated that, under acidic conditions, an increase in ionic strength and thus electrostatic interactions (that ultimately reduces the activity of ionic species), allows P to dissociate and solubilize (Ohlinger, Young & Schroeder, 1998; Tao, Fattah & Huchzermeier, 2016), otherwise the struvite solubility is minimal in pHs from 8 to 11 (Hanhoun et al., 2011; Cerrillo et al., 2015; Ren et al., 2015). Ashdec, in turn, contains Ca, nutrient which can be responsible for retrogradation in high pH environments, where P tend to precipitate as calcium phosphates, reducing/delaying its solubilization in the soil.

By looking at the daily accumulated P in leached solution (Figure 1B) it becomes clear that there is a strong correlation between P solubilization and solution pH variation in the soil. The solution pH is, therefore, a function of the type of dissolution reaction performed by each fertilizer and the intensity in which it occurs at a given moment.

Under TSP, the rapid decrease in pH at day one matched the immediate dissolution of P promoted by the fertilizer, that subsequently decreased until reaching its minimal daily solubilized P values in the last 10 days of incubation, along with its maximum pH values after day zero. Struvite showed similar behavior, once the decrease in pH match with the beginning of its P solubilization. Unlike TSP, its pH gradually reduced, never returning to its starting point, which means that more P could potentially be solubilized in a longer time.

In a study analyzing four struvite types (with different excess MgO), Degryse et al. (2017) concluded that both soil pH and excess base strongly affected the dissolution rate of all sources, being significantly greater in acidic conditions. When ground and mixed into the soil, the authors observed that struvite's agronomic effectiveness was comparable to that of monoammonium phosphate (MAP) for wheat (*T. aestivum*). Similarly, Horta (2017) showed in a pot experiment using an acidic soil (pH$_{H2O}$ = 5.1), that struvite presented similar ability to provide P for rye (*Secale cereale* L.) when compared to single superphosphate over 36 days. Talboys et al. (2016) also showed that the high amounts of organic acids exuded by buckwheat (*Fagopyrum esculentum* Moench) root system improved struvite solubility when compared to wheat (*T. aestivum*), which did not exudate as much.

These evidences demonstrate that plant activity, soil pH and fertilizer dissolution reaction characteristics are all factors playing crucial roles in struvite (and hazenite alike) solubilization dynamics. In our conditions, where there was no plant activity, it is safe to assume that the increase in pH promoted by hazenite and ashdec may have compromised their total P solubilization, once this is directly linked to the soil acidity for both sources (Tansel et al., 2017 & Watson et al., 2020).

3.3.2 Solubilized P

All treatments differed statistically from each other for leached P, except ashdec and control (Figure 2). The sources that presented most accumulated P solubilized after 60 days of incubation were TSP (52.8 mg col^{-1}), followed by struvite (29.7 mg col^{-1}), hazenite (15.5 mg col^{-1}), ashdec (0.38 mg col^{-1}) and control (0.02 mg col^{-1}). Besides the total amount of leached P, the moments and distribution of phosphate solubilization varied significantly between the sources (Figure 1B).
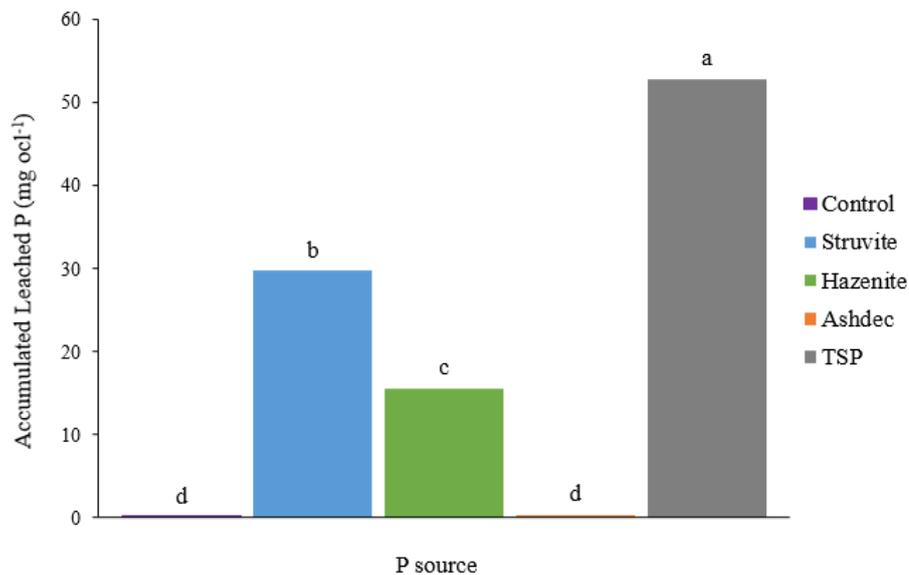
Figure 2. Total leached P in soil columns (mg col^{-1}) in 60 days under excess water addition, for the distinct phosphate sources. * Means followed by the same letter in the same harvest do not differ by 5% error probability in Tukey test.

Although TSP solubilized mostly of the composed P in 60 days, it is important to point out that this happened almost completely in a short spam (first 5 days) (Figure 1B). Commonly, TSP is applied at crop establishment, moment in which plant P demand is almost null. In this scenario, plants would not be able to absorb most of the solubilized phosphates, meaning that a large part of it will be potentially adsorbed into the colloidal fraction, becoming unavailable. According to Massey et al. (2009), highly water-soluble P sources tend

to release P too quickly to the soil solution, and may cause plant P deficiencies later on in the growing season.

On the other hand, Goto (1998) noticed that struvite's slow-release characteristic could be of interest specially in high P fixing soils, potentially providing more P for plants through time when compared soluble fertilizers such as TSP. Sutton et al. (1983) also stated that, struvite's slow P release rate may be closer to the plant's roots capacity of absorbing P, which may result in a greater P-use efficiency.

In our test, struvite had its peak in solubilization between days 36 and 56, decreasing afterwards (Figure 1B). This later and more gradual solubilization (peak lasting for 20 days, rather than five days observed for TSP) means a potentially greater uptake of P by plants, since at later stages crops are more developed and the root system is more able to capture it from soil solution.

Furthermore, while high pH levels tend to promote struvite crystallization, low pH increases its solubilization (Bhuiyan et al., 2008). For this reason, struvite may be considered a root activated fertilizer, once rhizosphere activity plays a major role in soil acidification, thus increasing the available P in this region (Hall et al., 2020). Being only slightly soluble in water (in this case 1.56%), it has been suggested that struvite's P release might be too slow to sufficiently supply early crop development (Talboys et al., 2015), stage in which P uptake is crucial for plant establishment and optimal yield (Boatwright & Viets 1966; Grant et al. 2001; Nadeem et al. 2011). Assessing that issue, Achat et al. (2014); Bonvin et al. (2015) reported no reduction in early P absorption compared to soluble sources when struvite was thoroughly mixed in the soil, and others such as Talboys et al. (2016), observed that the localized application of struvite significantly reduced P uptake when compared to soluble P fertilizers. Differences may be attributed to the differences in product composition, granulometry and application method.

Hazenite presented solubilization dynamics in between struvite and TSP (Figure 1B), reaching an intermediate level of P dissolution for a longer time, and not showing peaks of solubilization. Statistically, hazenite presented a higher P leaching than TSP and struvite from the 14th to the 24th day, after which it showed no difference to TSP, while solubilizing less P than struvite until the end (60 days). Its consistency in delivering P to the solution resides in its low standard deviation (SD = 0.181) in comparison to TSP (3.443) and struvite (0.774). Although hazenite accumulated leached P (15.51 mg col^{-1}) was only 52.2% of that released by struvite and 28.7% of that released by TSP (full period), the rhythm of P delivered to the solution is curious. Rather than immediately solubilizing most of the fertilizer P or

solubilizing virtually no P at the begging of the cycle, hazenite results were intermediary. Its P release dynamics is neither as late as struvite nor as early as TSP. In that sense, hazenite could be a viable option for a mid/late P supplier for plants.

Ashdec was the only source without statistical difference in leached P when compared to the control. Even though the water solubility of the ashdec fertilizer was the lowest among the four sources, its P solubilization was lower than anticipated. Besides that, this source also presents an expressive calcium concentration (9.6%) which, along with the high solution pH observed (7.69 ± 0.37) could also be, ultimately, contributing to retrogradation, reducing P solubility by its precipitation in solution as tricalcium phosphate. This reinforces the idea of ashdec being a fertilizer with virtually zero water solubility, in which its nutrients release should be induced by root exudates and soil microorganisms (Schaaf, 2017).

3.3.3   Soil P fractionation

In order to facilitate the comprehension and discussion of the distinct P pools in the soil, fractions were grouped by their lability. Details of each fraction can be accessed at the supplementary Table S2. For every lability, the majority of P from fertilizer sources was, unsurprisingly, found in the uppermost layer of the soil (0-1 cm), where the fertilizers were applied.

For soil labile P concentration (Figure 3A), struvite presented the greater values (7938 mg kg^{-1}), of this, more than 80% was allocated in the first layer. Next was hazenite (5877 mg kg^{-1}), with 77% in the first layer, ashdec (4468 mg kg^{-1}) with 84%, TSP (3821 mg kg^{-1}), presenting 63% of the total labile P in the 0-1 cm layer and, lastly, the control (26 mg kg^{-1}).

Soil Labile P (mg kg⁻¹)

Soil Moderately-labile P (mg kg⁻¹)

Soil Non-Labile P (mg kg⁻¹)

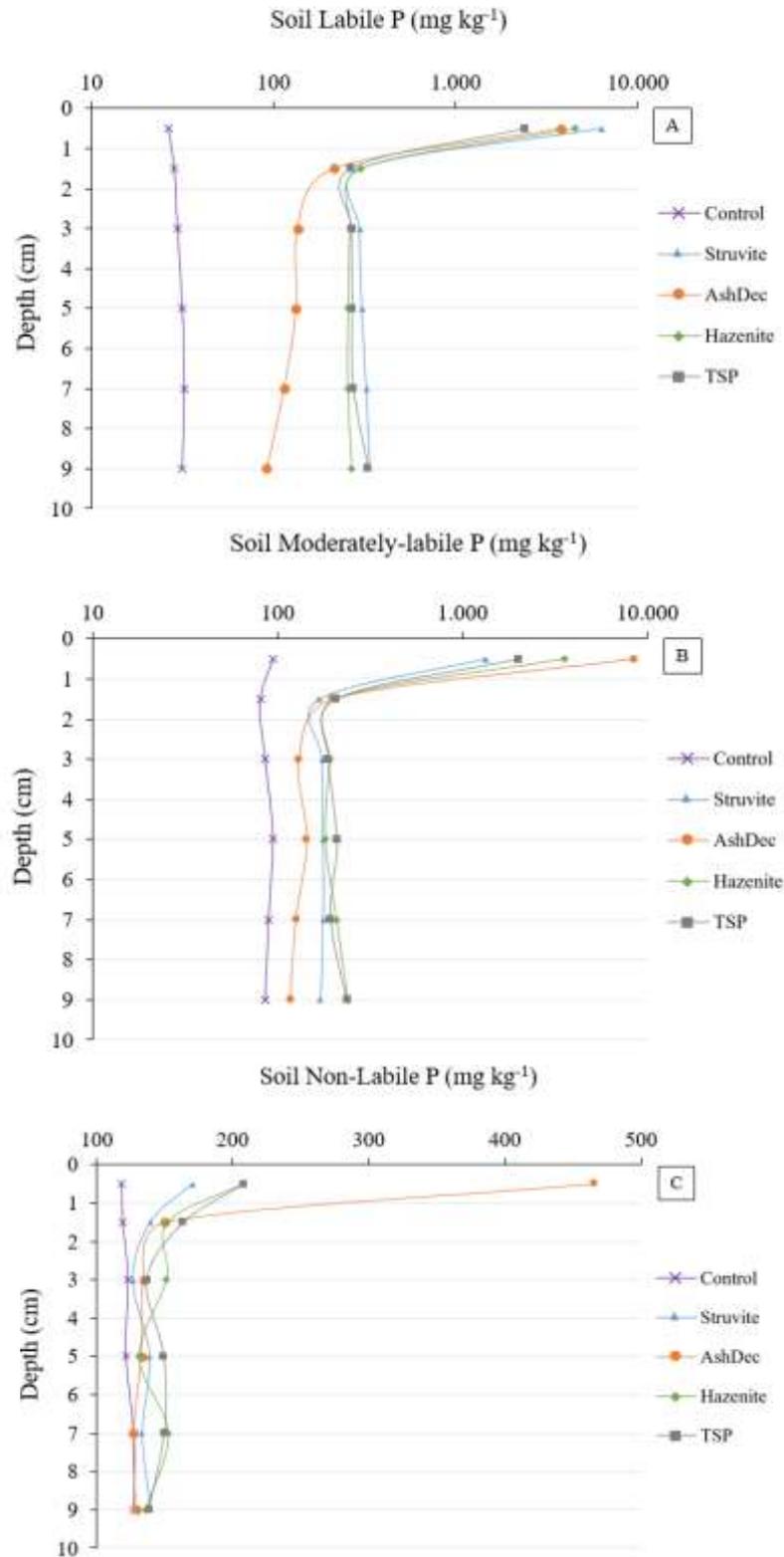Figure 3. Concentration (mg kg⁻¹) and distribution of labile P (A), moderately-labile P (B) and non-labile P (C) per depth under phosphate sources.

Although the concentration of labile P in deeper layers is similar between TSP, hazenite and struvite, TSP was responsible for diffusing the highest percentage of labile P from the first layer among all the tested sources (Figure 3A). After leaching almost 53% of

the total P added to the column, TSP also allowed nearly 37% of all fertilizer remaining as soil labile P to move down in deeper layers. Meanwhile, struvite and hazenite had similar behavior concerning P diffusion, allowing, respectively, 20 and 23% of the labile P to move below the 1 cm mark. Unlike TSP, however, the distribution of the leached P was more homogenous under hazenite and struvite, showing no difference in between the layers after the top-first (0-1 cm). This can be explained by the lower water-solubility of both fertilizers (in comparison to TSP), characteristic that hampers the phosphates diffusion in the soil.

Corroborating to our results, Nongqwenga et al. (2017), studying three contrasting soils under maize (*Zea mays* L.) cultivation, came to the conclusion that struvite's P release pattern in all three soils reached an equilibrium within 10 days of incubation, being readily available after that. Compared to single superphosphate (SSP), the capacity of struvite in supplying P demand for maize was soil specific, being most effective in a sandy soil with low extractable Fe and Al and overall low P fixating capacity. In another incubation trial, Horta (2017) similarly observed that in acidic soils, while struvite showed similar ability to provide P for plants than SSP, its late release could be overcome by applying struvite to the soil at least two weeks before seeding, as to induce P solubilization prior to plant demand. This is in agreement with the high labile P found under both struvite and hazenite by the end our study, which, after a certain delay in dissolution, were able to consistently solubilize phosphates to the soil solution.

For ashdec, only 16% of all labile P was able to reach deeper layers, decreasing gradually from 5% (1-2 cm) to 2% (8-10 cm). This clearly reinforces the low water-solubility of this source obtained in previous analysis (Table 2) and low P diffusion through the soil. On account of the low concentration of leached solution P accumulated by the ashdec along the 60 days of the experiment, it was expected that the biggest portion would be found in the labile P fraction in the soil, however, that was not the case. Struvite and hazenite both presented statistically higher accumulated leached P in 60 days and higher labile P concentrations in the soil when compared to the ashdec. Although ashdec presented significantly higher labile P in the topsoil (0-1 cm) when compared to the TSP, that amount alone would hardly be enough to match the amount of previously leached P in solution (Figure 2).

Despite low leaching and labile P delivered by ashdec, its use could still be beneficial under specific conditions, due to its potential to slowly solubilize its moderately-labile phosphate forms, which were the highest among all the studied sources (Figure 3B). The moderately-labile P fraction is the one that under the effect of rhizosphere's acid pH and the

action of phosphatase enzymes, could solubilize in order to supply plant demand. The amount of moderately-labile P accumulated in the soil from a fertilizer could point out its characteristic of late/slow release, once higher amounts of phosphates in this compartment could ultimately lead to a late cycle P supply or even aiming into subsequent years.

Ashdec was the source that presented the highest moderately-labile P levels per column (9214 mg kg^{-1}), with 62% of its total soil P being placed in that category (Figure 3B). This result reinforces the characteristics previously discussed about this source. Due to the nature of the bonds connecting the phosphates to the colloidal fraction, which grants it an intermediate energy level of adsorption, P solubility is lessened. At first, this enables the understanding of the low accumulated P concentration in the solution over the 60 days. Furthermore, ashdec consists of alkaline phosphate compounds, that promotes an increase in solution pH when solubilizing P through its alkaline reaction, as seen in figure 1A (Hermann & Schaaf, 2019). That, paired with the fertilizer calcium content and a scenario where no plant activity is available to balance the acidity in the system, it significantly reduces fertilizer P availability.

This hypothesis is supported by the major contribution of the HCl 1 mol L^{-1} extracted P in the total moderately labile P, representing more than 81% of the fraction (supplementary Table S2). These phosphates can be accessed over an intermediate- to long-time frame, along with a decrease in soil pH, root activity (with phosphate solubilizing enzymes) and with the depletion of the labile P in the soil (Touhami et al., 2020).

Hazenite was the second source to present great amount of moderately-labile P per column (4602 mg kg^{-1}), which represented over 40% of its total P. This result, reinforced by the labile P (51% of total P) justify the solubilization dynamics previously discussed. The source presents a high enough amount of labile P in order to rapidly deliver to the solution, being the fertilizer with the highest daily P solubilization in later stages (15th – 24th day). Otherwise, its accumulated leached P in 60 days was not even close to that achieved by struvite and TSP sources, a positive characteristic for environmental issues, explained by its relevant percentage of moderately-labile P pool. The relevance of both labile and moderately-labile P fractions in the soil treated with the hazenite, evidences its intermediate solubility behavior. It solubilized more P after 25-30 days (leached P; Figure 1B), and most of the P from fertilizer remained in the labile fraction. Furthermore, because of a significant proportion of P in the moderately-labile pool, it is expected that the fertilizer will still solubilize in long-term, potentially supplying plants demand in later stages or subsequent crop cycles.

Struvite presented the lowest values for moderately labile P per column amongst all sources (2195 mg kg^{-1}; Figure 3B). This may be explained by soil pH, along with its acid dissolution reaction, which permitted the second highest amount of leached P during the 60-day incubation period (Figure 2), also managing to maintain the highest labile-P among all treatments. Katanda et al. (2016) concluded that struvite presented greater potential for residual P availability for subsequent crops in a canola-wheat rotation when compared to MAP and a polymer coated MAP. The described "residual potential" may be due to its capacity of retaining more P in moderately-labile pool under certain soil/plant conditions. As the characteristics of both struvite and hazenite coincide in many ways, this conclusion could possibly be extended to the latter, especially in this particular case, due to hazenite's high moderately-labile P content in our results.

Strongly retained in the soil, either by high-energy bonds or as a part of mineral structure, the non-labile P is non plant available and may never become so due to its recalcitrant nature. Ashdec showed the highest results for non-labile P per column, followed by TSP, hazenite, struvite and control (Figure 3C). By subtracting the total non-labile P of each treatment from that found in the control it is possible to determine the quantity of non-available P coming from the fertilizers throughout the soil column, which represents 13, 21, 35 and 22% of the soil total P for struvite, hazenite, ashdec and TSP respectively. As seen in figure 3C, fertilizer played only a small part in the non-labile fraction in every source, meaning that most phosphate sources found their way into more labile compartments in the soil. Ashdec contributed the most to the total strongly adsorbed P.

One of the main goals of the ashdec industrial thermochemical process is improving the SSA's P bioavailability through the addition of $MgCl_2$ and other additives. This promotes the formation of magnesium and magnesium-calcium phosphates, which are more plant available than tri-calcium and aluminum phosphates present in the raw ash. However, pot and field experiments have shown that while the ashdec shows good performance on acidic soils, it performed poorly in alkaline and neutral environments (Adam et al., 2015). The comparably higher concentration of non-labile P present in the soil treated with ashdec might be explained by its primary source material (SSA), as well as by its Fe (6.2%) and Al (5.6%) content (Hermann & Schaaf, 2019; Smol et al., 2020). In non-calcareous environments, Fe and Al constitute the most important binding elements for P, forming stable compounds ($AlPO_4$ and $FePO_4$) which ultimately reduces P lability (Bortoluzzi et al., 2015). Even after considering source composition and soil conditions, the amount of non-labile P added via fertilizer is still minimal, only close to 2% of soil's total P.

All the while, struvite and hazenite showed the lowest contribution to non-labile P fractions, possibly due their composition and structure. This is an interesting result that helps the understanding of the potential of each of those fertilizers in supplying P in the short-, medium- and long-term. With different dynamics of solubilization and diffusion in the soil, the characteristics of the studied sources can be categorized as complementary, once they attend specific moments and demands of crops.

3.4 Conclusions

All three recycled phosphate sources (struvite, hazenite and ashdec) differed from each other and from the TSP in many ways. While TSP released the most P to the solution among all sources and did so very quickly, struvite and hazenite could be characterized as slow-release, increasing P dissolution considerably by the middle/end of the trial period. Ashdec presented very low P dissolution in the 60 days period, mainly due to its extremely low water solubility.

Struvite and hazenite presented the highest labile P concentration in the soil, an intermediate amount of moderately-labile P and the smallest amount of non-labile P. The majority of the recovered P from ashdec was found in the moderately-labile fraction, more specifically as Ca-P forms, explained by the pH increase promoted by its soil reaction with water, not dissolving or reprecipitating dicalcium phosphates present on it. For this reason, ashdec was not able to solubilize as fast as the other sources, being potentially more suitable in the long-term, especially in the presence of plants, to be evaluated in future studies. TSP presented low concentrations of both labile and non-labile P, and an intermediate level of the moderately-labile fraction, reaffirming its characteristic of early cycle P supplier.

The nutrient content and P solubility (water and citric acid) of the fertilizers in association with the solution data (pH and solubilized P) and the soil P pools were crucial for the understanding of the characteristics and dynamics of each fertilizer in the trial conditions. By correlating all the gathered information, it was possible to have a clear picture of how these fertilizers work in a controlled environment, which might serve as a basis for the comprehension of their behavior under plant presence.

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SUPPLEMENTARY DATA
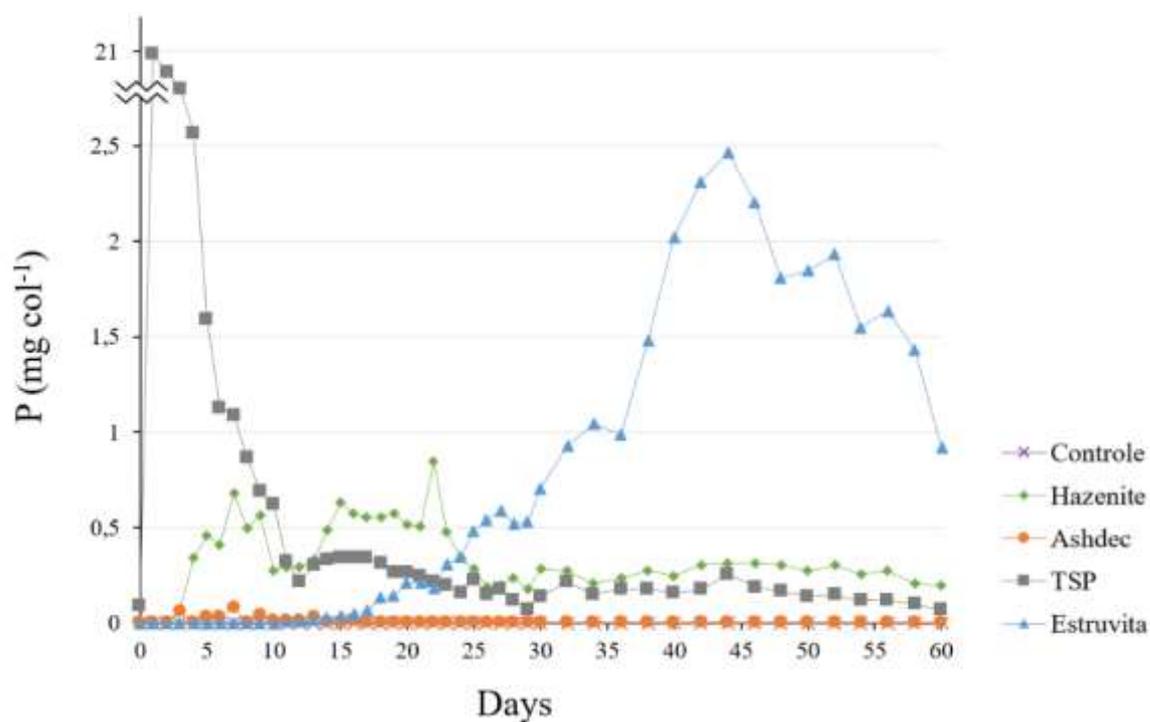
Figure S1. Daily solubilized P (mg col^{-1}) under distinct fertilizer sources and water addition.

Table S1. Total P in the soil and added via fertilizer sources, soil original P and solution recovered P per column and relative recovery percentage.

Treatments	Total P	Soil fractions recovered P	Solution leached P	Total recovered P	P recovery rate
		mg col^{-1}			%
Control	12.15	12.13	0.02	12.15	100
Struvite	112.15	79.69	29.70	109.40	97.50
Hazenite	112.15	94.62	15.51	110.13	98.20
AshDec	112.15	107.55	0.38	107.93	96.23
TSP	112.15	56.12	52.80	108.92	97.12

Table S2. Soil P fractions specified by extractor and total P per depth under distinct fertilizer sources incubated for 60 days.

Treatment	Labile			Moderately-Labile			Non-Labile			Total
	Resin	$NaHCO_{3(i)}$	$NaHCO_{3(org)}$	$NaOH\ 0.1_{(i)}$	$NaOH\ 0.1_{(org)}$	HCl	$NaOH\ 0.5_{(i)}$	$NaOH\ 0.5_{(org)}$	Residual	Total
					$P\ (mg.kg^{-1})$					
					0 - 1 cm					
Control	2.4	5.9	18.3	28.3	57.0	10.0	16.4	26.7	75.3	240.3
Struvite	2078.0	1293.4	3008.2	252.8	1042.5	32.6	27.3	31.3	112.1	7878.1
AshDec	772.1	620.7	2387.3	202.7	923.9	7373.2	221.3	88.8	156.0	12746.1
Hazenite	646.6	1324.9	2556.0	239.9	3094.2	239.9	52.7	40.3	114.5	8309.1
TSP	151.2	232.2	2028.9	425.9	1167.2	425.9	64.0	22.8	121.5	4639.6
					1 - 2 cm					
Control	2.4	6.2	19.7	26.3	46.2	8.0	16.2	24.9	78.1	228.1
Struvite	182.0	104.6	9.9	103.1	50.4	14.8	22.9	28.6	88.1	604.4
AshDec	131.6	64.9	17.7	84.0	37.8	75.5	26.3	31.8	92.2	561.9
Hazenite	160.0	109.6	31.3	148.8	30.9	25.8	28.0	33.0	90.9	658.3
TSP	116.1	120.7	27.6	142.1	48.7	15.2	21.9	40.3	101.4	634.1
					2 - 4 cm					
Control	2.4	6.9	20.2	27.2	49.0	8.9	16.1	27.0	80.0	237.9
Struvite	158.3	103.9	34.9	111.2	47.8	15.7	22.6	19.5	84.4	598.2
AshDec	65.2	53.4	17.2	76.7	39.8	13.7	21.9	29.0	83.6	400.4
Hazenite	127.6	107.4	30.8	136.0	32.9	22.0	25.2	40.1	86.2	608.2
TSP	119.9	121.3	26.9	151.2	21.1	16.4	22.5	21.7	92.8	593.7
					4 - 6 cm					
Control	2.6	6.5	22.4	29.8	48.9	15.8	15.8	27.8	77.9	247.6
Struvite	171.6	105.6	28.4	119.2	36.1	21.6	20.4	31.8	86.8	621.7
AshDec	49.7	56.8	26.3	83.1	40.9	20.1	20.3	30.9	81.8	409.9
Hazenite	105.5	108.4	43.8	139.0	15.5	26.8	24.1	28.4	79.2	570.5
TSP	127.5	123.9	18.4	147.1	40.7	21.4	21.8	38.1	89.4	628.2
					6 - 8 cm					
Control	2.4	6.5	23.3	32.1	44.0	13.2	15.0	32.4	80.2	249.1
Struvite	196.2	105.0	22.6	123.1	33.8	20.3	23.1	29.9	80.5	634.6
AshDec	33.4	46.4	34.4	69.8	41.3	14.9	20.1	30.3	76.6	367.3
Hazenite	106.5	109.9	40.2	156.7	30.5	22.8	27.3	47.4	78.4	619.6
TSP	133.9	114.3	26.6	143.3	31.4	19.3	24.8	42.8	82.3	618.7
					8 - 10 cm					
Control	2.5	6.8	22.4	28.3	49.1	8.8	16.4	30.4	80.5	245.1
Struvite	195.5	101.3	39.2	111.6	36.0	22.5	22.0	31.7	86.2	646.0
AshDec	20.1	29.3	42.2	55.1	43.4	18.8	19.5	31.0	78.7	338.0
Hazenite	98.8	115.3	54.9	160.3	42.1	38.0	27.1	31.3	77.9	645.7
TSP	152.4	135.9	43.9	163.7	41.2	32.4	23.9	35.1	79.4	707.8

4 AGRONOMIC RESPONSE OF SUGARCANE UNDER PHOSPHATE SOURCES RECYCLED FROM WASTEWATER AND SEWAGE SLUDGE

Abstract

The recycling of phosphorus (P) from wastewaters and sewage sludge can produce fertilizers with low water-solubility, potentially increasing the relative P efficiency (RPE) and agronomic efficiency (RAE) of sugarcane in comparison to TSP (chosen as conventional source). This study aimed to evaluate the agronomic potential of three recycled fertilizers (struvite, hazenite and ashdec) compared to TSP in three P doses (30, 60 and 90 mg kg^{-1}). Two consecutive cycles of sugarcane, 90 days each, were conducted in a sandy clay loam Ferralsol inside a greenhouse. At both harvests, biometric parameters (number of sprouts, plant height and stem diameter) and dry mass yield (DMY) were measured, shoot nutrient content (N, P, K, Ca, Mg and S) was determined and soil P fractionation was done. The impacts of each treatment in the soil chemical characteristics and their potential on sugarcane production were also evaluated. An increase in DMY and P uptake by sugarcane was promoted by struvite (both harvests) and hazenite (90 d) compared to other sources, while ashdec performed comparably to TSP. Higher RPE and RAE were also observed for struvite and hazenite in the lowest doses, but all three recycled sources performed very similar to TSP in these parameters. Furthermore, our soil P data disclosed higher levels of labile P for all recycled sources in the first cycle, while TSP was the only source under which the non-labile P pool was increased by the end of the experiment.

Keywords: *Saccharum* spp., Phosphate recycling, Struvite, Wastewater, Sewage sludge, P speciation, Agronomic potential, Fertilizer efficiency.

4.1 Introduction

Sugarcane (*Saccharum* spp.) is a strategical crop due to its flexibility in producing sugar and ethanol according to market prices and demand. Brazil is the largest sugarcane producer worldwide, responsible for the production of 642 million tons of sugarcane in 2019/2020 (CONAB, 2020) and has been growing at an accelerated pace, more than doubling its planted area from 2001 to 2009 (MAPA, 2019) and increasing 14.3% from 2009 to 2019 (Miranda & Martinho, 2021). One of the most important factors restraining Brazilian sugarcane productivity is the low phosphorus (P) availability present in most soils in the country, with high capacity of P-fixation, reducing fertilization efficiency (Soltangheisi et al., 2019). To overcome these issues and supply plants demand, large amounts of inorganic phosphate fertilizers are used annually, leaving behind a large P footprint (Roy et al., 2016; Withers et al., 2018). This scenario is concerning, since both P scarcity and an increase in phosphate rock prices (as observed in 2008, with an increase of over 800%) could ultimately endanger Brazilian sugarcane production by making it unsustainable and/or financially impracticable (Mew, 2016).

The currently phosphate fertilizers added in Brazilian sugarcane production are mostly highly water-soluble, usually applied at crop establishment, and cover applications are often reduced or overlooked due to its believed low plant response (Rossetto et al., 2002; Vitti & Mazza, 2002; Soltangheisi et al., 2019). Nevertheless, alternative slow-release fertilizers could be used as P sources (Soltangheisi et al., 2019). Struvite, hazenite and ashdec are

considered slow-release P fertilizers, and while the first two can be obtained through chemical precipitation of wastewaters (O'Neal & Boyer, 2015; Watson, 2020), the latter is produced via thermochemical treatment of the sewage sludge ashes (SSA) (Hermann & Schaaf, 2019).

Struvite ($MgNH_4PO_4 \cdot 6H_2O$), and hazenite ($KNaMg_2(PO_4)_2 \cdot 14H_2O$) are P sources recycled through chemical precipitation of wastewaters that could serve as alternative phosphate fertilizers (Clemens & Oeppert, 2018). Besides being environmentally friendly, they present low water-solubility, reducing P fixation in the colloids and thus being potentially more effective in agricultural systems than conventional fertilizers (Yang et al., 2011; Cabeza et al., 2011; Watson et al., 2020). Moreover, the incineration of sewage sludge into SSA and its thermochemical treatment can also recover P, by degrading some alkaline compounds under high temperatures and promoting the reaction of phosphates with added salts, generating bioavailable P compounds while also evaporating toxic trace elements. Through this process, the ashdec fertilizer ($CaNaPO_4$) is generated, a concentrated and citrate-soluble P fertilizer that can be directly applied onto fields (Hermann & Schaaf, 2019).

Our hypothesis is that struvite, hazenite and ashdec, as recycled P sources, are more efficient phosphate fertilizers, reducing P adsorption in agricultural soils and supplying crop P requirements more effectively when compared to conventional sources. The objectives were to evaluate the efficiency and residual effect of these three recycled sources in short-term sugarcane P supply compared to the commercial fertilizer triple superphosphate (TSP), assessing their forms in the soil in two 90 days' consecutive cycles, while understanding how it affected sugarcane's growth and development, along with soil chemical parameters.

4.2 Materials and methods

The experiment was conducted in a greenhouse at the "Luiz de Queiroz" College of Agriculture (ESALQ/USP), Piracicaba – SP. The study compared TSP to three distinct sources recycled from German wastewater treatment plants (WWTPs), in partnership with the German Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und -prüfung - BAM), the Berlin Centre of Competence for Water (Komptenzzentrum Wasser Berlin - KWB), and Outotec GmbH & Co.KG. The tested sources were struvite and hazenite, both precipitated from wastewaters (supplied by KWB), and AshDec®, a fertilizer co-developed by BAM and Outotec, from the thermochemical treatment of sewage sludge ash (SSA).

The chosen crop was sugarcane (*Saccharum* spp.) once it is vastly cultivated in Brazil and has a vigorous root system with great capacity to explore the whole soil volume. The

variety was RB96-6928 due to its high response to P fertilization reported in previous study (Arruda et al., 2016). Establishment was done by transplanting 4-weeks-old pre-sprouted seedlings from a substrate (rice straw) to pots filled with 6 kg of dried, sieved and fertilized soil (distinct treatments). Before transplanting, the seedling roots were washed with tap water. The experiment was conducted for two cycles of 90 days each, after first cycle the shoot was harvested and their sprouts left for another cycle.

4.2.1 Soil characterization and fertilization

Soil was collected from the surface layer (0-20 cm) of a grassland area, classified as a sandy clay loam Ferralsol (FAO, 2014), with very low P availability (Raij et al., 1997). The soil was air-dried and sieved using a 2 mm mesh sieve. Its chemical and textural characterization is shown in Table 1. As pH was low and Ca and Mg levels were also limiting for sugarcane, $CaCO_3$ and $MgCO_3$ were added to elevate the Ca level to 20 $mmol_c$ dm^{-3} and Mg level to 8 $mmol_c$ dm^{-3}, incorporated homogeneously. Potassium was also homogeneously added to the soil via KCl (50 mg kg^{-1}), aiming to supply the initial demand of the sugarcane. Moreover, complementary K and S were supplied via K_2SO_4 surface fertilization 50 days after establishment, using more 50 mg kg^{-1} of K and 16 mg kg^{-1} of S.

Table 1. Soil chemical and textural parameters before experimental setup.

pH $CaCl_2$	O.M.	P_{resin}	S	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	H + Al	SB	CEC	V	m
-	g kg^{-1}	mg kg^{-1}		--------------------$mmol_c$ kg^{-1}---------------------							%	
4.9	16	5	6	<0.9	13	5	12	16	18.8	34.8	54	10
				Clay	Silt	Sand						
				---------g kg^{-1}---------								
				201	11	788						

O.M = Organic matter; SB = Sum of bases; CEC = Cation exchange capacity; V = Base saturation; m = Al saturation.

Nitrogen was added via NH_4NO_3, in the dose of 150 mg kg^{-1} divided in three similar applications, at 25, 50 and 75 days after establishment. The composition of the fertilizers used for each treatment are presented on Table 2. The N content of struvite and K content of hazenite were discounted to maintain equity in total nutrients applied.

After the first harvest, 50 mg kg^{-1} of N and K and 16 mg kg^{-1} of S were applied to all pots. Moreover, another 50 mg kg^{-1} of N was added 30 days after that, using the same previously mentioned source. For micronutrients, boron, zinc and copper were added via H_3BO_3 (0.8 mg kg^{-1}), $ZnSO_4$ (4 mg kg^{-1}) and $CuSO_4$ (1.3 mg kg^{-1}) respectively, diluted in 100

mL of water and applied at 25 days after establishment. All fertilizer doses were defined according to Sousa (2004) recommendation. Fertilizers were diluted in water before application.

Each experimental unit was composed of an 8 L pot filled with 6 kg of soil. Plants were watered daily, maintaining 60 - 70% of the soil's maximum water holding capacity (MWHC) throughout the whole duration of the experiment. The greenhouse temperature was kept within the range of 30 °C during the day and 18 °C at night.

4.2.2 Treatments

The tested sources were struvite, hazenite, ashdec, and TSP. Their nutrient content is described on Table 2. For the four sources, three P doses were administered (30, 60 and 90 mg kg^{-1}) based on their total P_2O_5 content. One control treatment (nil-P) was added for comparison, resulting in a total a (4 x 3) + 1 design, for a total of 13 treatments. Pots were distributed in randomized blocks with four replicates. The three recycled sources as well as TSP were applied at establishment, the latter being used as a positive control.

Table 2. Nutrient content of fertilizers sources composing the treatments for pot trials.

Fertilizers	K	Ca	Mg	N	Na	P_2O_5 total	P_2O_5 water	P_2O_5 HCi
	---------------------------------%---------------------------------							
Struvite	-	-	8.3	6.0	-	28.7	1.5	28.4
AshDec	0.8	9.5	1.5	-	11.0	16.6	0.7	15.6
Hazenite	7.1	-	7.3	-	-	24.7	3.3	24.3
TSP	-	10.0	-	-	-	45.0	40.5	45.0

Water = water-soluble; HCi = soluble in citric acid 2%.

4.2.3 Sampling procedures and measurements

Sugarcane development was evaluated in two cycles of 90 days each (90 and 180 days after establishment). After the first cycle, the aboveground biomass was harvested for dry mass yield (DMY) and nutrient tissue content determination. Plants' sprouts were left for regrowth for another 90 days and harvested again for the same analyses. Right before the first and second harvest, biometric measurements were taken, including cane thickness, plant height and number of sprouts.

The shoot DMY of both harvests were obtained after drying in an oven at 60°C. Shoot material was milled at 1 mm, then sulfuric digestion was done for nutrient content determination (Tedesco et al., 1995). Once digested, the material was tested for its P content

by the phosphomolybdate blue method (Murphy and Riley, 1962) using a probe colorimeter at 882 nm. Nitrogen content was determined by distillation in alkaline solution by micro-Kjeldhal method, collected in boric acid 4%, and then titration by sulfuric acid solution. Potassium content was determined by flame photometry, while Ca, Mg e S were determined by atomic absorption spectrophotometry. Accumulated nutrient in tissue (mg pot^{-1}) was estimated by considering the nutrient concentration (N, P, K, Ca, Mg and S) in each harvest, multiplied by each shoot dry mass.

Moreover, the relative agronomic efficiency (RAE) and the relative P efficiency (RPE) of the recycled sources were estimated by comparing the accumulated (sum of both harvests) DMY and shoot P, respectively, to that of TSP, as done by Vogel et al (2015). The formulas for RAE% and RPE% (I and II) are expressed below:

$$\text{I.} \qquad RAE\% = \frac{DMY\ promoted\ by\ Recycled\ Source}{DMY\ promoted\ by\ TSP}\ x\ 100$$

$$\text{II.} \qquad RPE\% = \frac{Shoot\ P\ promoted\ by\ Recycled\ Source}{P\ uptake\ promoted\ by\ TSP}\ x\ 100$$

Soil was sampled right after each harvest (90 and 180 days) in order to verify the nutrient availability (P, K, Ca and Mg). The determinations were done according to Raij et al. (2001). Furthermore, subsamples were submitted to P fractionation as described by Hedley et al. (1982), modified by Rheinheimer (2000). The data was grouped in labile (extracted by anion-exchange resin and NaHCO$_3$ 0,5 mol L^{-1}), moderately-labile (extracted by NaOH 0,1 mol L^{-1} and HCl 1 mol L^{-1}) and non-labile P (NaOH 0,5 mol L^{-1} and residual P) for a more comprehensive discussion. Resin extracted soil macronutrients (Ca, Mg, K and P) was also done at both harvests just to assess the soil chemical characteristics through the experiment. The data is available in the supplementary table S1.

4.2.4 Statistical Analyses

All data were subjected to the normality test (Shapiro-Wilk) and subsequently to analysis of variance (two-way ANOVA) to compare means at the same harvest. Means were compared through Tukey test. Regression analysis was also performed in order to describe the effects of P dose and the interaction dose x source for the variables analyzed. We evaluated linear and quadratic models and selected the best one for each variable based on the coefficient of determination (R^2) and model significance (P > F). All the analyses were

performed in the R statistical software considering p ≤ 0.05 as cut-off for statistical significance.

4.3 Results and Discussion

4.3.1 Sugarcane biometric parameters

The plant parameters evaluated (number of sprouts, height and stem diameter) at both harvests are presented in Table 3. While P source affected most variables (except number of sprouts at 180 d) in comparison to control, minor differences were observed between the fertilized treatments for the same harvest, whilst no interaction of source x dose was present. Overall, all three recycled sources were comparable to, or outperformed TSP. Although all treatments were performed in a similar pot condition, is important to emphasize that pot size may have limited plant growth and "homogenized" the biometric results, which can ultimately contribute to a reduction or delay in development, masking certain treatment effects (Kiaer et al., 2013). Moreover, sugarcane is a plant well known for its great capacity of overcoming stressful scenarios, which might have also contributed for a similar growth and development irrespective of doses and fertilizers (Grivet et al., 1996; Grivet & Arruda, 2001).

Table 3. Sugarcane biometric parameters (stem diameter, plant height and number of sprouts) at 90 and 180 days after establishment, under phosphate sources and doses.

Stem diameter (cm)										
	90 d (first harvest)					180 d (second harvest)				
Source	P dose (mg kg^{-1})					P dose (mg kg^{-1})				
	0	30	60	90	Mean	0	30	60	90	Mean
Control	1.27	-	-	-	1.27c*	0.92	-	-	-	0.92b
Struvite	-	1.51	1.48	1.58	1.52ab	-	1.70	1.93	1.93	1.85a
Hazenite	-	1.56	1.56	1.56	1.56a	-	1.88	1.80	1.83	1.83a
Ashdec	-	1.34	1.56	1.29	1.39bc	-	1.73	1.80	1.80	1.77a
TSP	-	1.35	1.51	1.45	1.43abc	-	1.73	1.88	1.88	1.82a
Mean	1.27ns	1.44	1.52	1.42	-	0.92b	1.75a	1.85a	1.85a*	-

*y = -0.0002x² + 0.0304x + 0.9515
R² = 0.967

Plant Height (cm)										
	90 d (first harvest)					180 d (second harvest)				
Source	P dose (mg kg^{-1})					P dose (mg kg^{-1})				
	0	30	60	90	Mean	0	30	60	90	Mean
Control	70.5	-	-	-	70.5c	33.0	-	-	-	33.00b
Struvite	-	115.2	117.3	114.7	115.7a	-	82.75	94.00	93.25	90.00a
Hazenite	-	101.0	103.2	111.6	105.2ab	-	86.63	87.25	87.50	87.12a
Ashdec	-	104.7	116.0	96.5	105.7b	-	78.13	91.25	94.50	87.95a
TSP	-	110.8	104.7	113.6	109.7ab	-	83.00	100.25	83.00	88.75a
Mean	70.5b	107.9a	110.3a	109.1a*	-	33.0b	82.62a	93.18a	89.56a*	-

*y = -0.0107x² + 1.359x + 72.07   *y = -0.0148x² + 1.9318x + 34.244
R² = 0.956   R² = 0.987

Number of Sprouts										
	90 d (first harvest)					180 d (second harvest)				
Source	P dose (mg kg^{-1})					P dose (mg kg^{-1})				
	0	30	60	90	Mean	0	30	60	90	Mean
Control	0.0	-	-	-	0.0b	2.75	-	-	-	2.75ns
Struvite	-	1.50	4.25	3.75	3.16a	-	3.25	2.00	2.00	2.41
Hazenite	-	2.00	1.50	3.50	2.33a	-	2.00	1.50	2.75	2.08
Ashdec	-	2.50	2.00	3.50	2.66a	-	2.75	2.50	2.00	2.41
TSP	-	3.00	3.00	2.50	2.83a	-	3.00	1.00	3.00	2.33
Mean	0.0b	2.25a	2.68a	3.31a*	-	2.75ns	2.75	1.75	2.43	-

*y = -0.0005x² + 0.075x + 0.101
R² = 0.967

* Means followed by the same letter in each column or line do not differ by 5% error probability in Tukey test. ns = non-significant.

For stem diameter, significantly higher values were observed at the second harvest in comparison to the first. Source affected stem diameter at 90 d, when higher values were observed for hazenite compared to ashdec, and only hazenite and struvite differed from the

control. At 180 d, all sources performed similarly and were better than control. The P dose did not impose an effect in stem diameter, being only higher than control in the second harvest. This indicates that P dose was possibly not a detrimental factor for stem diameter when resin extracted soil P was at least 5 mg kg^{-1}, however, after the first harvest, the resin-P was reduced to 2 mg kg^{-1}, and the control was much lower compared to all other fertilized treatments. Similarly, field experiments developed by Caione et al. (2011) and Albuquerque et al. (2016) in different regions of Brazil concluded that P dose did not impose significant effect on sugarcane stem diameter.

Fertilizer source influenced plant height at 90 d, when struvite outperformed ashdec and all fertilized treatments were higher than control. At 180 d, all sources and doses performed similarly, differing only from the control. Overall, plant height was lower in the second harvest in comparison to the first. Caione et al. (2015) also observed no effect of P dose in sugarcane height.

The growth of grasses, root development, number of sprouts and overall productivity is usually highly affected by P availability (Santos, 2002). As proved here, the number of sprouts was significantly affected by P fertilization at 90 d, when all treatments differed from the control. However, no differences between fertilizer source or dose were observed for this parameter. The lack of differences in plant sprouts between the control and other treatments at 180 d may be due to the capacity of the sugarcane cultivar RB96 6928 in adapting to low soil-P conditions, as has been suggested by Arruda et al. (2016). Santos et al. (2009) also concluded that P source did not influence the number of sprouts.

Sugarcane DMY was also not affected by the interaction P source x dose in both harvest periods, showing only effect of each factor individually (Figure 1A, B), and was considerably higher at the second harvest for all treatments (except control), being on average 30.9% higher than observed in the first harvest. An explanation is that the root activity and residual organic acids exuded from the first season could promote a higher solubilization of phosphates, which were readily absorbed by the already established root system at sprouting, as suggested by Talboys et al., (2016) and by Hermann & Schaaf (2019), to be an important factor for both struvite and ashdec solubilization. This could also explain the higher speed in which plants grew up in the second season.
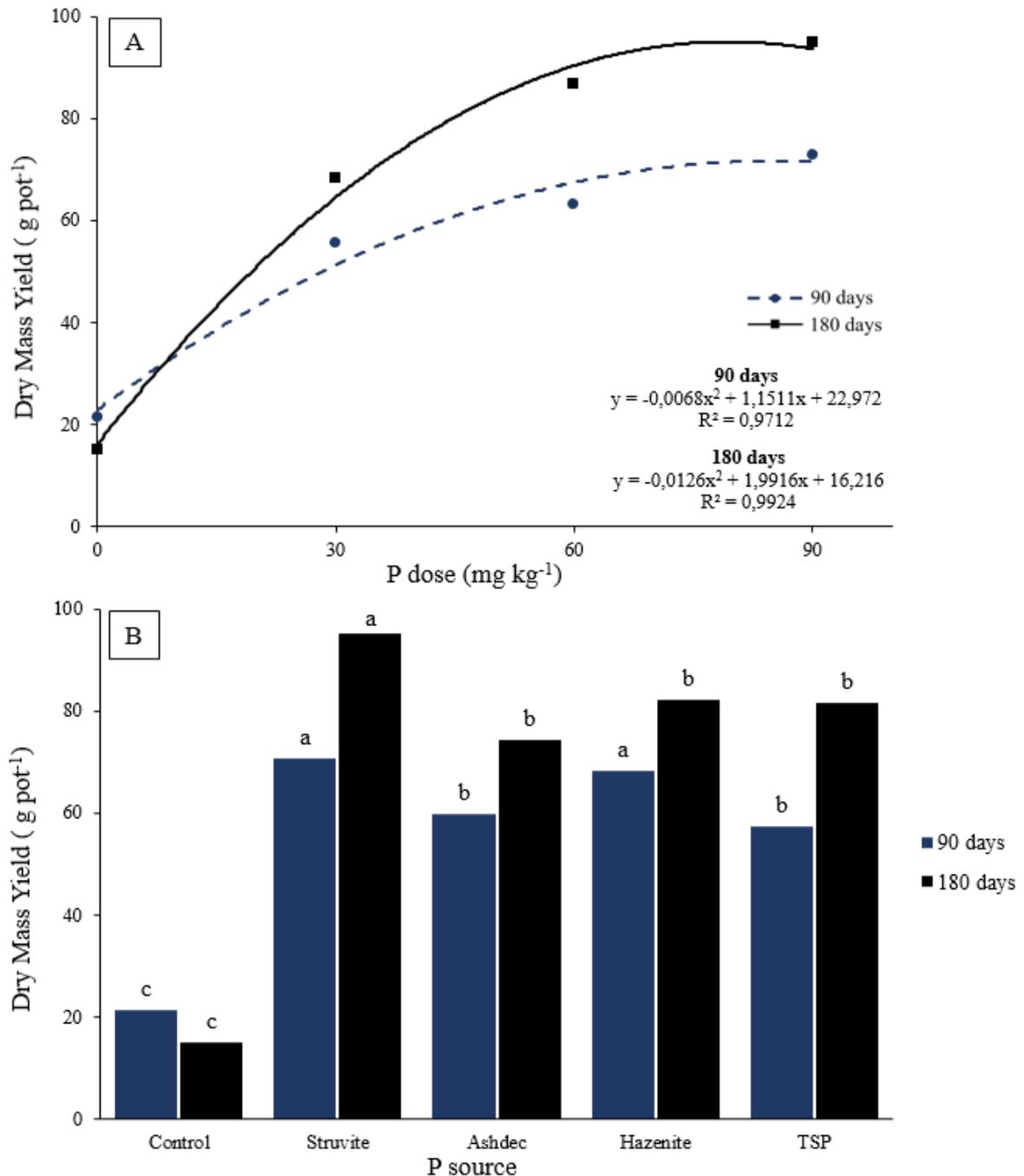
Figure 2. Sugarcane Dry Mass Yield (g pot^{-1}) as affected by doses (A) and sources (B) of recycled phosphate sources at 90 and 180 days after seedlings establishment. * Means followed by the same letter in the same harvest do not differ by 5% error probability in Tukey test.

A positive correlation between doses and DMY was seen at both harvests for all sources (Figure 2A). Usually in Brazil, phosphate fertilizers are added into the furrow during sugarcane planting, and doses can be as high as 180 kg ha^{-1} P_2O_5 under adequate soil P level (Rein et al., 2015). Moreover, in cases of low soil P level, a fertilizer P correction is also recommended before planting, varying from 80 to 300 kg ha^{-1} P_2O_5, normally added onto the soil surface and incorporated in full soil volume (0-20 cm) (Sousa and Korndörfer, 2011), which, in total, corresponds to the addition of approximately 39.3 to 104.8 mg kg^{-1} P. The

optimal doses for DMY found in our experiments were 84.6 and 79.0 mg kg^{-1} at 90 and 180 d respectively, which are consistent with the P correction and fertilization rates described in the literature by authors such as Morelli et al. (1991), Gama (2007), Mendonça et al. (2015) among others.

Significant differences in DMY were observed between sources (Figure 2B), since struvite was responsible for the highest DMY at both harvests, being only comparable to hazenite at 90 d. At 180 d, struvite outperformed all other sources, while those only differed from the control. Higher DMY production and the effectiveness of struvite compared to water-soluble P sources was also reported by Katanda et al. (2016) on canola, by Barak et al. (2006) and Gell et al. (2011) on corn, while Massey et al. (2009) and Rech et al. (2019) reported a similar performance by different struvites compared to TSP on spring wheat and soybean respectively. Moreover, Severin et al. (2014), in a pot experiment comparing types of treated sewage sludge ashes (SSAs) to TSP in maize, also reported similar yields for all treatments, although the SSAs showed slower plant development than TSP, as we also found in our trial.

The relative agronomic efficiency (RAE) of sugarcane under the recycled sources in relation to TSP considering both seasons (90 and 180 d) is presented on Table 4. Struvite and hazenite performed on average 20.3% and 9.7% respectively better than TSP, while ashdec underperformed by 3.3%. However, statistical differences were only found in the smaller dose, where struvite was higher than TSP and ashdec, while hazenite outperformed the latter. Huygens and Saveyn (2018) reported through a meta-analysis that struvite's RAE was comparable to that of mined and synthetic P sources considering multiple crops and fertilizer types, while Watson et al. (2020) found that hazenite performed comparably to TSP in this regard for *Lollium multiflorum* L., both corroborating to the results obtained here.

Table 4. Relative Agronomic efficiency (RAE%) of recycled fertilizer sources and doses related to TSP in sugarcane's dry mass yield during two consecutive cycles of 90 d each.

Fertilizer	P dose (mg kg^{-1})			Mean
	30	60	90	
Struvite	128.3a*	118.6abc	114.0abcd	120.3
Hazenite	121.1ab	105.6abcd	102.4bcd	109,7
Ashdec	92.4d	100.7bcd	97.0cd	96,7
TSP	100.0bcd	100.0bcd	100.0bcd	100.0
Mean	110.45	106.2	103.3	

* Means followed by the same letter do not differ by 5% error probability in Tukey test.

4.3.2   Plant nutrient concentrations

The shoot P accumulated by sugarcane was affected by P source and dose at both 90 and 180 d evaluations (Figure 2A, B) but not by their interaction, similar to what was observed for DMY. Plants treated with struvite and hazenite were more efficient than those under TSP and ashdec in absorbing P at 90 d (Figure 2B). At 180 d, most plants were capable of absorbing significantly more P in comparison to 90 d, as consequence of a better plant growth as previously mentioned, and only struvite was more efficient than ashdec in this regard, while all treatments performed significantly better than control on both harvests. Possibly, TSP solubilized its P too quickly, when plants were not yet fully established and, thus, its root system was not able to promptly absorb it. This allows a premature adsorption of orthophosphates into the soil solid phase, ultimately reducing their plant availability, later accessed when roots were more developed (second season). Contrariwise, ashdec's slower solubilization might also have been a detrimental factor in its performance, delaying P availability, ultimately reducing plant growth and shoot P.
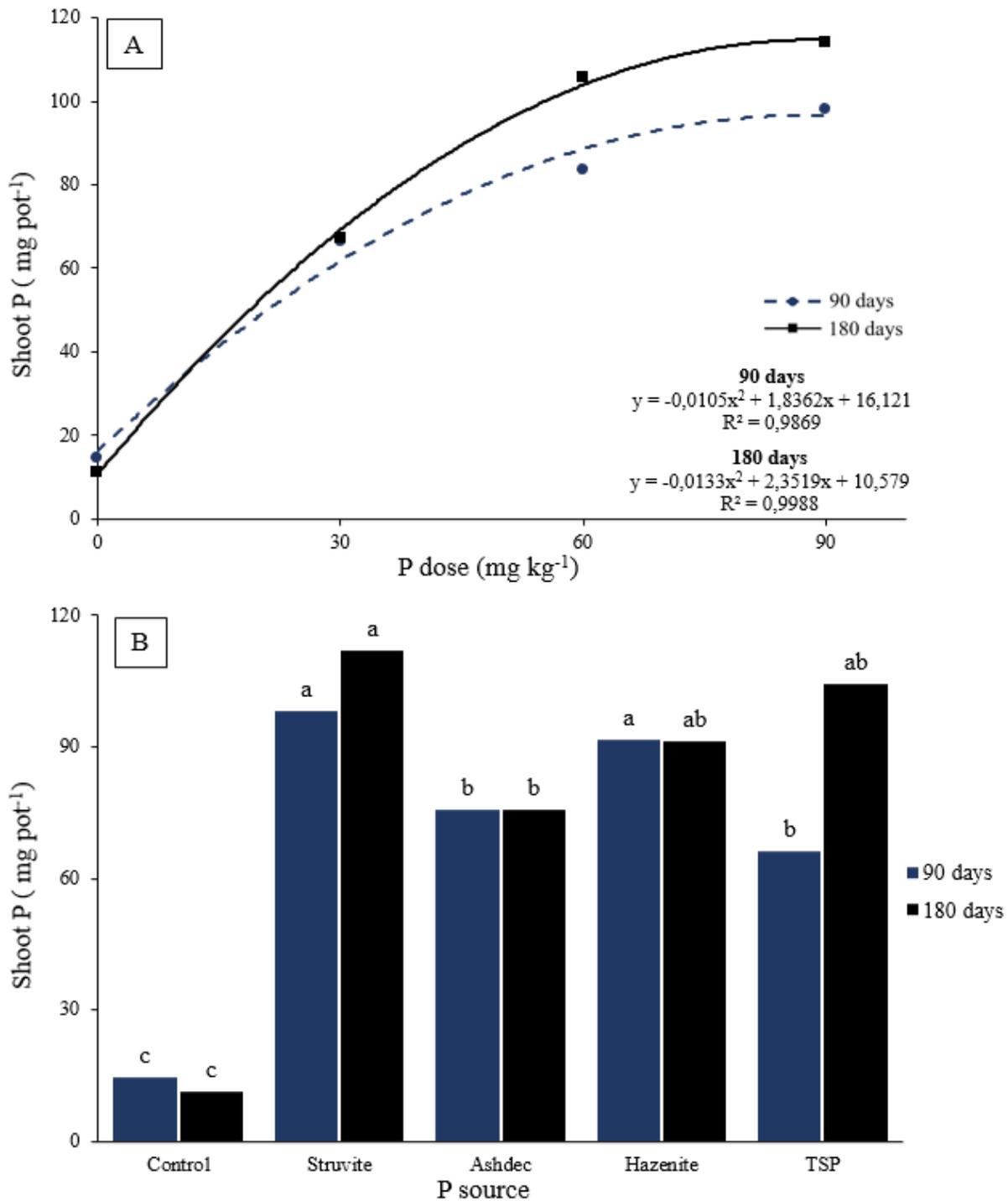
Figure 2. Sugarcane shoot P (mg pot^{-1}) as affected by doses (A) and sources (B) of recycled phosphate sources at 90 and 180 days after seedlings establishment. * Means followed by the same letter in each harvest do not differ by 5% error probability in Tukey test.

The relative P efficiency (RPE) of the recycled sources in relation to TSP, considering here the sum of both periods (90 and 180 d), is presented on Table 5. On average, struvite was 37.7% more efficient than TSP in accumulating sugarcane shoot P by over the course of the experiment. Hazenite was 20.8% more efficient than TSP and ashdec was 5.8% less efficient than TSP, similar to the pattern found for the RAE (Table 4). This same trend was reported by

Vogel et al. (2017), who observed that, in a field scenario using forage rye, struvite had an RPE 10% higher than TSP, while SSAs tested underperformed by 4 to 9%, and by Vogel et al. (2015) in a greenhouse scenario using five different crop species, where struvite's RPE was up to 19% higher than TSP, while SSAs were 1.3 to 6.9% lower. In our trial, however, differences are found only in the smaller dose, where struvite and hazenite are significantly more efficient than ashdec and TSP. Franz (2008) also reported that plants fertilized with sources derived from SSA showed similar P absorption compared to commercial superphosphates for three different plant species.

Table 5. Relative P efficiency (RPE%) of recycled fertilizer sources and doses related to TSP in sugarcane's shoot P during two consecutive cycles of 90 d.

Fertilizer	P dose (mg kg^{-1})			Mean
	30	60	90	
Struvite	173.0a*	121.7bc	118.3bc	137.7
Hazenite	152.1ab	111.8c	98.6c	120.8
AshDec	96.4c	93.5c	92.6c	94.2
TSP	100.0c	100.0c	100.0c	100.0
Mean	130.3	106.7	102.3	

* Means followed by the same letter do not differ by 5% error probability in Tukey test.

Although struvite, hazenite and TSP allowed comparable shoot P in the higher doses, struvite's DMY was significantly higher than under hazenite (90 d) and TSP (both harvests). This is due to P being one of the plant macronutrients with the lowest use efficiency in terms of DMY production (Borges et al., 2019). Possibly, plants were capable of accumulating and storing P rather than metabolizing it, not being fully effective in its use (Marschner, 2012). For this reason, the shoot accumulation of the other macronutrients by sugarcane was addressed, giving an overall idea of their nutritional state throughout the trial, as well as the impact of fertilizer composition in plant absorption. Nutrients were differently affected by source, dose and their interaction in each harvest. Only the significant effects for each period were represented in Figure 3, while non-significant ones were not shown.
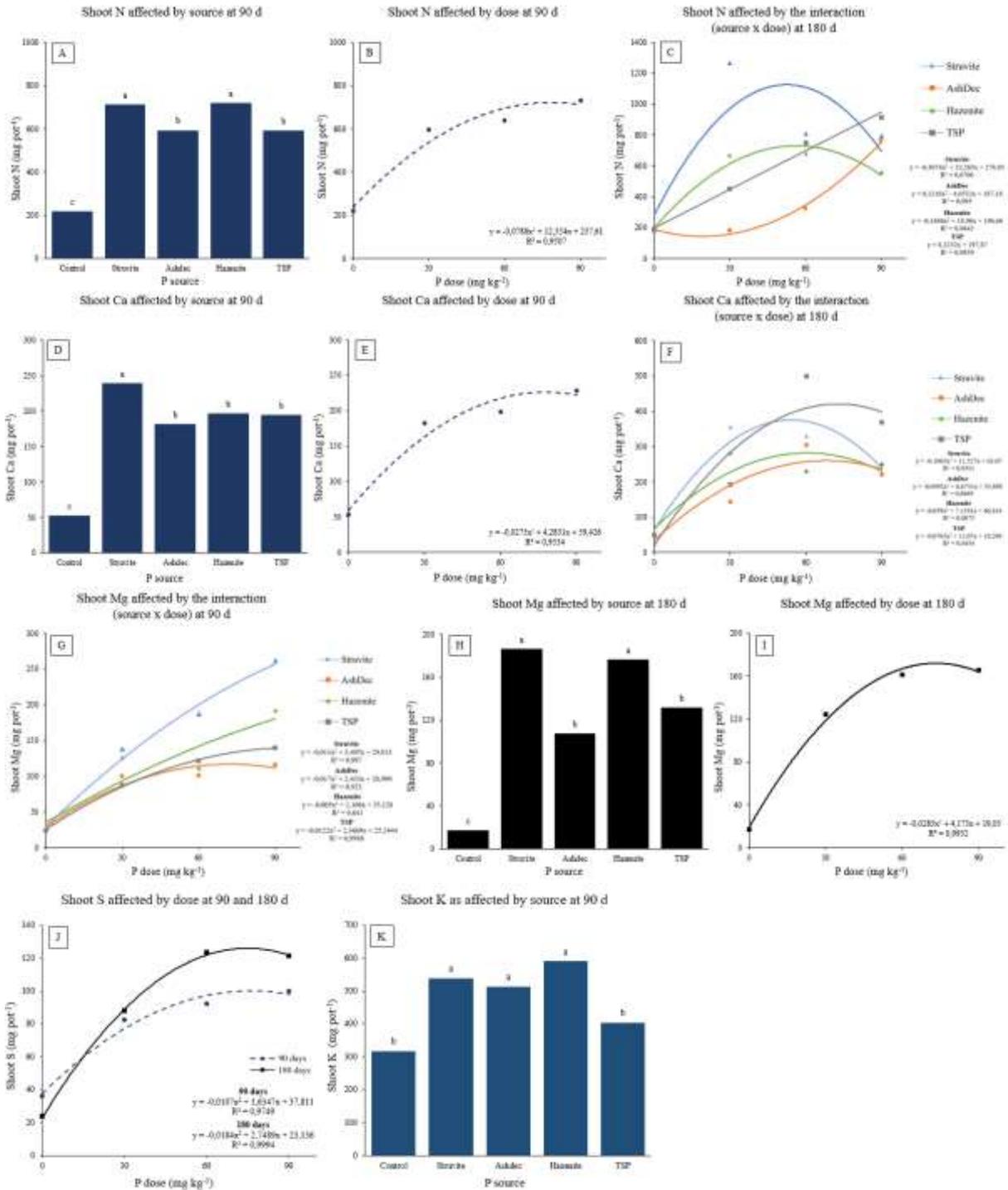
Figure 3. Shoot nitrogen (A, B and C), calcium (D, E and F), magnesium (G, H and I), sulfur (J) and potassium (K) (mg pot^{-1}) when affected by source, dose or their interaction at 90 and/or 180 d after establishment. * Means followed by the same letter for the same variable do not differ by 5% error probability in Tukey test.

Struvite allowed greater shoot N than TSP and ashdec at 90 d, also being more efficient at 180 d in most doses. Calcium absorption was significantly higher in the struvite treatments in comparison to all others at 90 d, while at 180 d, it outperformed ashdec and hazenite but allowed less shoot Ca than TSP. For shoot Mg , struvite managed to better supply plants when compared to all other sources at 90 d, being comparable only to hazenite at 180 d,

which may be due to its Mg content (8.3%) and the slower solubilization characteristic, more aligned with plants demand. The differences in shoot N, Ca and Mg could have also been influenced by greater root growth and development due to higher P absorption, that allowed plants to explore more soil volume, as well as by the synergistic effect between P and Mg/Ca absorption, due to root growth promoted by P and the ionic balance of cations and anions uptake (Merhaut, 2007). Only shoot K was not influenced by dose, however source impacted its absorption, since all three recycled fertilizers showed higher shoot K than TSP at 90 d, which may be due to the more vigorous growth and P absorption (in the case of struvite) and also by the K content and release dynamics of the hazenite and ashdec fertilizers.

The differences in shoot Mg between struvite and hazenite sources could be explained by hazenite's K content, once K has been reported to inhibit root to shoot transport of Mg, although the opposite was not yet strictly observed, possibly due to higher specificity of some K transporters in comparison to Mg, which may also allow some K uptake (Gransee & Führs, 2013). Vogel et al. (2017) also reported greater forage rye and sorghum growth in field conditions under struvite in comparison to TSP. This superior result was attributed to the positive Mg effect observed in the struvite treatment. In our work, struvite allowed higher shoot N, Ca, Mg and K by sugarcane plants than TSP which could have led to the higher DMY.

4.3.3 Soil P fractionation

For better comprehension, soil P fractions were discussed here by lability. The complete data of soil P fractionation discerned by each extractor (and organic or inorganic forms) is available on supplementary Table S2. The labile P pool was affected by the interaction source x dose at 90 d (Figure 4A), but only by source (Figure 4B) and dose (Figure 4C) individually at 180 d. In the first season (90 d), TSP was responsible for the lowest labile P levels compared to the other sources in the same doses, while struvite tended to outperform both TSP and hazenite in this regard at higher doses, being comparable to ashdec. In the second season (180 d), there was a general depletion of labile P (Figure 4B, C) in relation to 90 d, explained by plant uptake. At this time, all sources showed comparable levels of labile P directly correlated with dose, only differing from control.
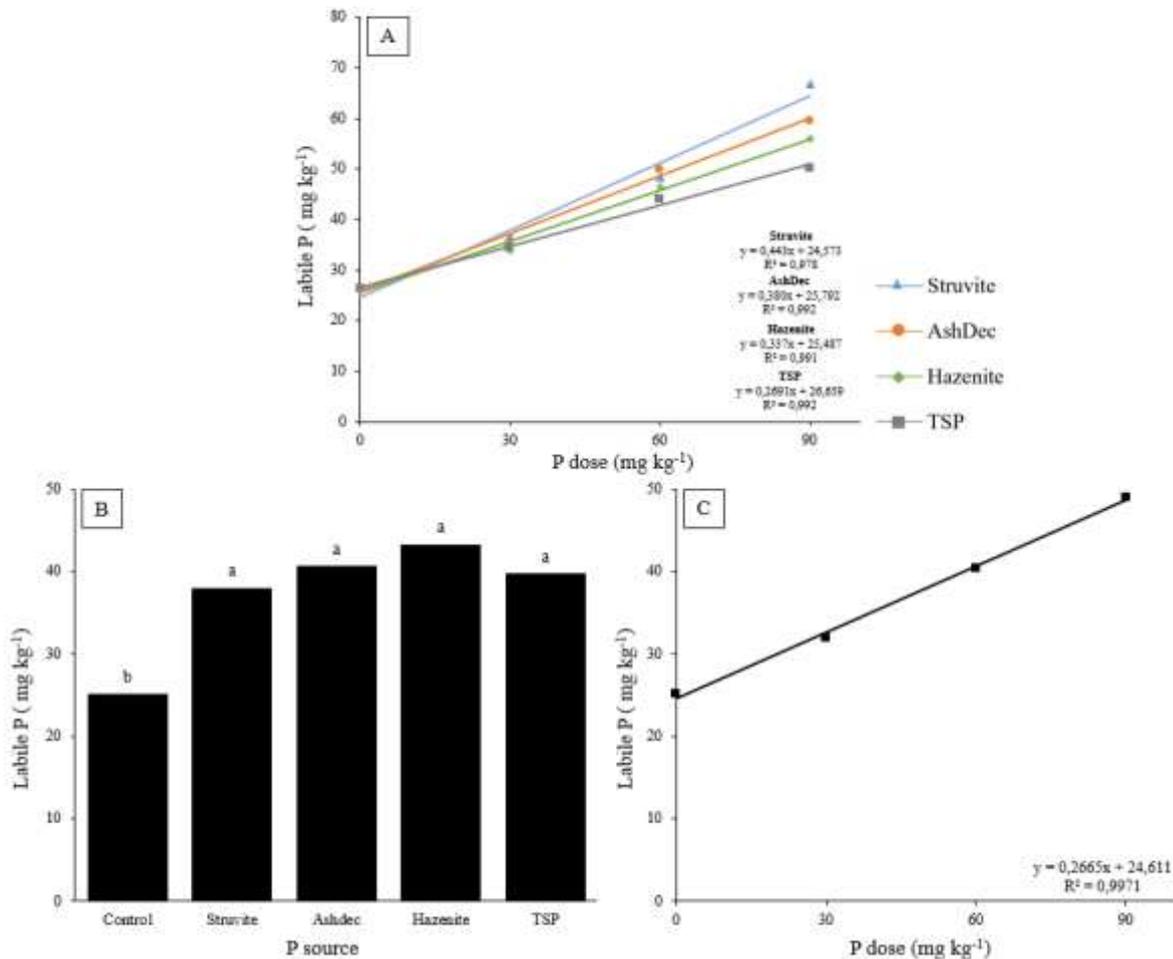
Figure 4. Soil labile P (mg kg^{-1}) as affected by the interaction source x dose at 90 d (A) and individual effects of source (B) and dose (C) at 180 d after establishment. * Means followed by the same letter do not differ by 5% error probability in Tukey test.

Similar results were found by Vogel et al. (2017) for soils cultivated with spring barley, where linear correlation of the effect of struvite, TSP and two types of SSA (including a Ca-SSA similar to ashdec) were observed, considerably increasing the soil labile P pool. In their study, however, significantly higher values of soil labile P were found for struvite in comparison to the Ca-SSA treatment, which was not the case in our trial. Although the labile P is readily available for plant uptake, if not rapidly absorbed it will be adsorbed to the soil with time due to soil-fertilizer interactions, especially in soils with high Fe/Al oxi(hydroxides) content, ultimately decreasing P availability (Bortoluzzi et al., 2015; Fink et al., 2016). This happens with the "aging" and the increase in the adsorption energy of the P bonds between these oxides, which ultimately ends up turning labile into moderately-labile and those into non-labile P if no contrary pressure is imposed upon the system, such as rhizosphere and microorganism's activity (Wang et al., 2013; Yoon et al., 2014).

The soil moderately-labile P levels are presented in Figure 5. Moderately-labile P was affected by the interaction source x dose at 90 d, and by dose only at 180 d. Higher values

observed under ashdec at 90 d could be explained by its original material composition. Sewage sludge often presents low P bioavailability depending on its characteristics, soil and plant used in experiments (De Haan, 1980; Pommel, 1981; Sikora et al., 1982; McCoy et al., 1986). The AshDec® thermochemical process has as its main objective to increase the bioavailability of these P compounds over time (Hermann & Schaff, 2019). However, during this process some phosphates remain in moderately-labile forms, such as Ca-P, and thus the addition of ashdec to the soil might have had a direct impact on this specific fraction.
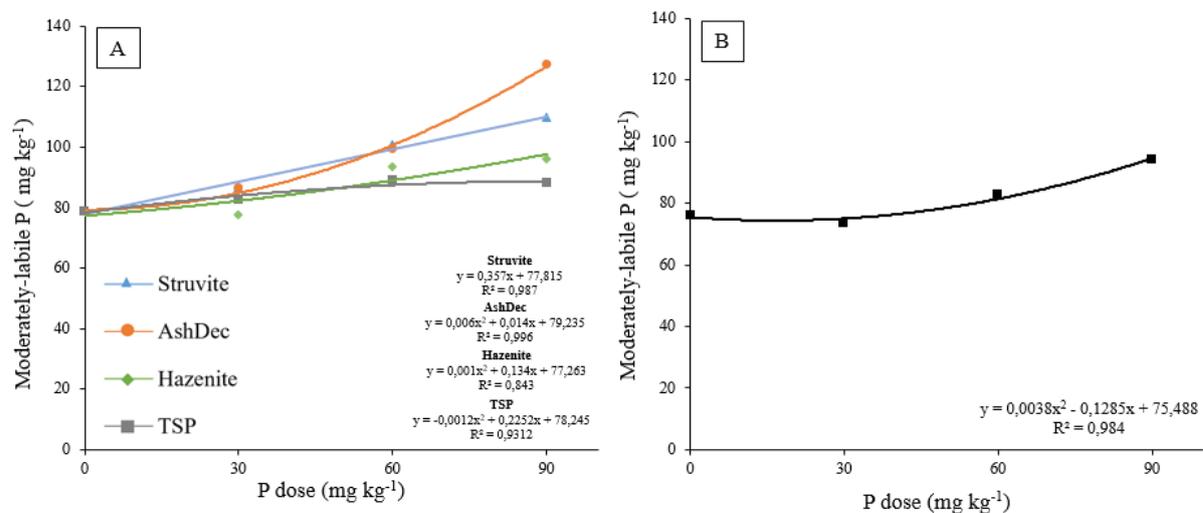

Figure 5. Soil moderately-labile P (mg kg^{-1}) as affected by the interaction source x dose at 90 d (A) and by dose only at 180 d (B) after establishment.

At 180 d, the moderately-labile P diminished considerably for all sources, meaning that this fraction has contributed to P dissolution and thus to plant uptake. Different authors have pointed out that even relatively low solubility P compounds can be mobilized in the soil through crop and microorganism activity (Requejo and Eichler-Löbermann, 2014; Dakora and Phillips, 2002; Eichler-Löbermann, 2007), which can explain this moderately-labile P reduction between crop cycles. Ashdec presented a particularly greater reduction on this P pool, no longer differing from other treatments at 180 d, meaning that it managed to find its way into the labile fraction, possibly due to rhizosphere effect, which reinforces the proposition that this fertilizer is particularly affected by plant activity (Hermann & Schaaf, 2019).

The non-labile P was the pool that presented the highest values among all labilities throughout all treatments and both harvests. This characterizes the soil as highly P-sorptive and shows that a great amount of its total P is bonded to soil colloids with high energy. This fraction was the less affected by the treatments at 90 d, where no effect of source nor dose

was observed. However, the source x dose interaction influenced the soil non-labile P at 180 d (Figure 6). No statistical differences were observed between any of the treatments (including control) at 90 d and only TSP diverged significantly from other treatments at 180 d. This is possibly due to the fact that the addition of fertilizers tends to accumulate more labile-P forms in the short-term, while the non-labile P is more related to the soil characteristics than fertilizer sources and/or doses (Gatiboni et al., 2007), what may be altered in a long-term management.

This would also explain the source x dose interaction effect observed at 180 d, when there is an increase in non-labile P compared to 90 d for most doses under TSP. At first, only a small percentage of the fertilizer reacted and bonded to the soil, which means that nearly all non-labile P comes from soil characteristics, and not from the added fertilizers. However, as time progresses, more fertilizer derived P became bonded with high energy, thus increasing the correlation between non-labile P and the treatments. Along this line, it is reasonable to assume that the longer these distinct treatments are observed, the higher the correlation between them and the non-labile P would become, due to a vast array of reactions taking place between soil and fertilizer.

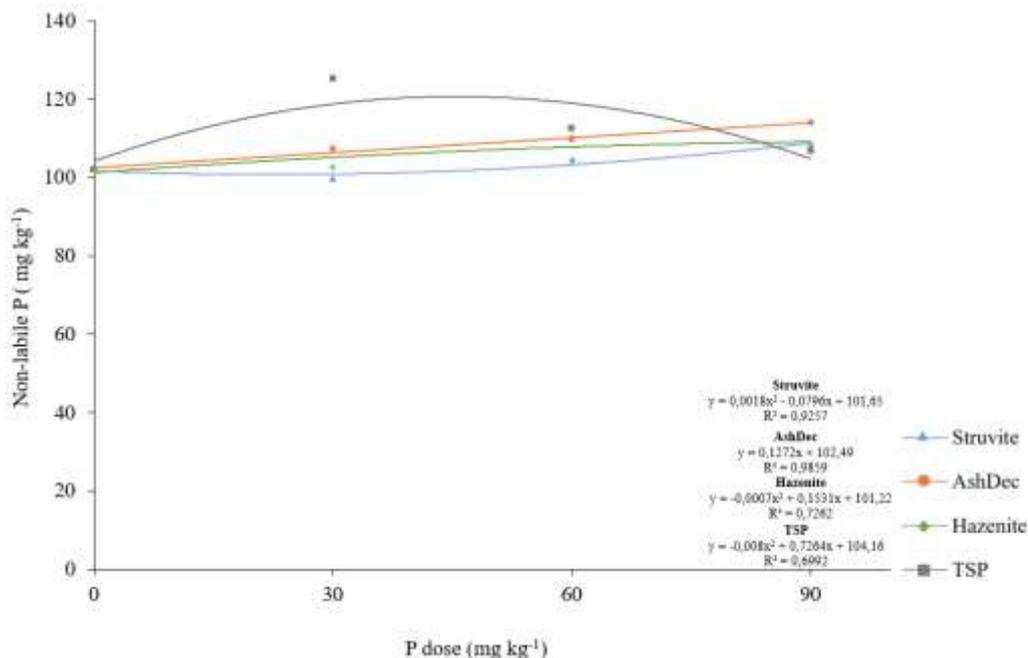Figure 6. Soil non-labile P (mg kg^{-1}) at 180 d after establishment, under phosphate sources and doses.

Analyzing the bioavailability of soil P forms for multiple successions (lasting from 30 to 45 days each) of different crops, Gatiboni et al. (2007) stated that while the residual P did not suffer major alterations until the 9th cycle, great depletion was observed between the 12th

and 15th cycles for different species. This shows that although the residual P was preserved while the moderately-labile fraction was able to supply the P absorbed from the labile fraction, in situations of high P scarcity, all fractions of P may take part in solubilizing the element to the soil solution, including the more recalcitrant P forms, corroborating to our findings. Although treatment effect on the non-labile P pool was very subtle, it was possible to observe a pattern of reduction of this fraction between periods, signalizing that some of these phosphates are released to the moderately-labile fraction. The only exceptions were the TSP that showed a slight increase in the non-labile P at 180 d when compared to the 90 d values. This was expected for TSP once its high water-solubility and asynchrony with plants demand could ultimately cause P adsorption to the soil colloids, possibly becoming less available overtime.

4.4 Conclusions

Overall, P dose was more detrimental in the increase of sugarcane development than fertilizer source in a 180 days' pot trial. Struvite and hazenite allowed higher DMY by sugarcane than TSP and ashdec at 90 days, and struvite outperformed all sources at 180 days. Struvite and hazenite also performed significantly better than TSP and ashdec in accumulated shoot P at 90 days, but only ashdec was significantly worse than struvite at 180 days.

Struvite and ashdec delivered more labile P in the first 90 days when compared to TSP and hazenite. No differences between fertilizers were found in the end of both cycles (180 days) in soil labile P, showing that the fertilizer dynamics influence diminished over time. Ashdec was the only fertilizer that impacted the moderately-labile soil P fraction at 90 days, which matches the fertilizer late release characteristics. However, due to its low initial P release, ashdec did not allow good plant initial development at the lowest dose, and therefore did not perform as well as the other recycled sources in terms of fertilizer efficiency.

Fertilizer source and dose had no effect on the non-labile P pool in the first 90 days, however their interaction impacted it at 180 days, where TSP allowed a significant increase on that non-soluble fraction. This compartment presented an overall reduction between the first and the second harvest, meaning that in certain scenarios it might participate into increasing soil moderately-labile and posteriorly labile P.

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SUPPLEMENTARY DATA

Table S1. Resin extracted nutrients in the soil at 90 and 180 days after establishment, under phosphate sources and doses.

Source	P dose	90 days				180 days			
		P	Ca	Mg	K	P	Ca	Mg	K
	mg kg^{-1}		mmol$_c$ kg^{-1}			mg kg^{-1}		mmol$_c$ kg^{-1}	
Control	0	3.7	17.5	5.7	1.6	2.8	17.3	2.2	0.5
Struvite	30	20.7	14.2	6.1	0.3	14.5	8.1	1.0	0.0
Hazenite	30	22.6	25.0	6.0	0.5	15.1	2.8	0.7	0.2
AshDec	30	20.8	21.7	5.3	0.4	19.0	14.3	1.1	0.4
TSP	30	21.9	15.5	4.5	0.2	24.3	5.2	1.0	0.0
Struvite	60	30.3	14.8	6.3	0.4	23.3	13.9	0.8	0.0
Hazenite	60	31.0	21.0	6.0	0.3	29.1	7.6	3.0	0.0
AshDec	60	31.0	23.8	4.8	0.4	24.9	13.2	1.8	0.0
TSP	60	28.5	12.0	3.5	0.3	28.9	4.0	0.5	0.0
Struvite	90	43.4	14.3	6.5	0.4	29.9	11.4	3.8	0.1
Hazenite	90	40.5	27.8	7.5	0.4	32.3	5.8	1.8	0.0
AshDec	90	45.9	25.7	6.3	0.2	36.5	15.0	2.9	0.0
TSP	90	33.6	15.4	3.4	0.3	31.9	5.4	0.7	0.0

Table S2. Soil P fractions specified by extractor and total P at 90 and 180 days.

Source	P dose	Labile			Moderately-Labile			Non-Labile			
		Resin	NaHCO$_{3(i)}$	NaHCO$_{3(org)}$	NaOH 0.1$_{(i)}$	NaOH 0.1$_{(org)}$	HCl	NaOH 0.5$_{(i)}$	NaOH 0.5$_{(org)}$	Residual	Total
		P (mg.kg^{-1})									
		90 days									
Control	0	2.0	9.8	14.7	31.0	35.4	12.3	16.2	13.6	75.2	210.2
Struvite	30	7.3	15.8	13.5	38.4	35.5	12.5	16.3	14.6	83.7	237.5
Struvite	60	11.7	23.5	13.1	48.0	38.1	14.6	17.7	14.0	81.9	262.6
Struvite	90	21.0	27.3	18.7	58.6	36.1	14.8	17.4	14.8	80.2	288.9
AshDec	30	5.4	15.0	15.1	38.0	33.5	14.8	17.3	15.0	77.7	231.7
AshDec	60	12.2	22.5	15.3	49.9	32.2	17.1	21.0	14.4	90.1	274.7
AshDec	90	18.2	31.3	10.1	68.2	30.8	28.1	23.5	15.1	83.2	308.5
Hazenite	30	6.7	13.6	13.6	34.2	31.7	11.9	20.1	15.2	70.0	217.0
Hazenite	60	11.5	21.3	13.6	48.9	31.2	13.4	16.6	12.0	96.4	264.8
Hazenite	90	16.3	25.6	14.1	54.3	28.1	13.7	16.9	12.2	86.7	267.9
TSP	30	5.2	15.0	14.1	37.3	32.2	12.9	16.7	14.4	80.4	228.3
TSP	60	10.0	20.1	14.1	44.8	30.6	13.5	17.6	11.1	82.2	243.9
TSP	90	12.8	22.1	15.3	45.2	31.5	11.6	16.8	11.4	81.9	248.5
		180 days									
Control	0	1.5	9.4	14.2	30.1	35.4	10.5	14.5	10.4	77.2	203.1
Struvite	30	3.5	12.9	15.1	35.9	31.2	11.0	14.8	8.6	76.2	209.4
Struvite	60	6.3	19.6	10.5	45.5	28.6	11.3	15.5	8.9	79.9	226.1
Struvite	90	10.5	26.7	8.8	50.8	31.8	13.1	16.1	9.1	83.2	250.2
AshDec	30	4.7	12.5	15.8	36.1	19.0	11.2	15.8	10.7	80.7	206.4
AshDec	60	6.5	18.8	14.4	46.6	15.5	14.4	16.5	11.3	81.9	225.9
AshDec	90	12.8	24.8	11.7	54.9	24.6	20.9	20.8	12.0	81.2	263.6
Hazenite	30	3.2	11.1	18.4	33.7	36.9	10.6	14.0	12.8	75.9	216.7
Hazenite	60	8.1	18.4	17.7	41.6	34.1	11.7	15.9	11.9	82.4	241.9
Hazenite	90	11.9	24.5	16.7	49.3	31.0	12.6	16.5	13.1	78.7	254.3
TSP	30	2.6	16.2	11.5	37.6	20.1	11.4	16.3	12.2	96.6	224.5
TSP	60	7.7	21.6	12.2	44.5	25.3	12.2	16.8	11.1	84.7	236.2
TSP	90	10.7	29.0	7.5	52.8	20.9	14.1	17.9	10.6	78.4	242.0

5   FINAL CONSIDERATIONS

We aimed to evaluate the agronomic potential of P sources recovered from wastewater and sewage sludge, as well as understanding the reasons behind differences found in sugarcane production when compared to a conventional source.

The leaching columns experiment enlightened various characateristics of the recycled sources P dissolution, behavior and speciation in the soil, which enhanced the comprehension of these fertilizers and guided the discussion throughout the work.

Greenhouse experiments are very fitting for the study of the P dynamics of recycled fertilizers in the soil, due to the controlled conditions and short duration when compared to sugarcane field experiments.

Future field experiments could compliment the data reported in this work by showing how open field conditions may affect the performance of the recycled sources.