Recovered phosphorus for a more resilient urban agriculture: Assessment of the fertilizer potential of struvite in hydroponics

Verónica Arcas-Pilz [a,1], Martí Rufí-Salís [a,b,1], Felipe Parada [a], Anna Petit-Boix [c], Xavier Gabarrell [a,b,*], Gara Villalba [a,b]

[a] Sostenipra Research Group (SGR 01412), Institute of Environmental Sciences and Technology (CEX2019-000940-M), Z Building, Universitat Autònoma de Barcelona (UAB), Campus UAB, 08193 Bellaterra, Barcelona, Spain
[b] Department of Chemical, Biological and Environmental Engineering, Universitat Autònoma de Barcelona (UAB), Campus UAB, 08193 Bellaterra, Barcelona, Spain
[c] Chair of Societal Transition and Circular Economy, University of Freiburg, Tennenbacher Str. 4, 79106 Freiburg i. Br., Germany

HIGHLIGHTS

- Struvite is tested in hydroponic production of *Phaseolus vulgaris*.
- Yield, water fluxes, and P balances are analysed.
- More yield is produced by plants with more than 5 g of struvite.
- Slow release by struvite decreases the leached P.

GRAPHICAL ABSTRACT
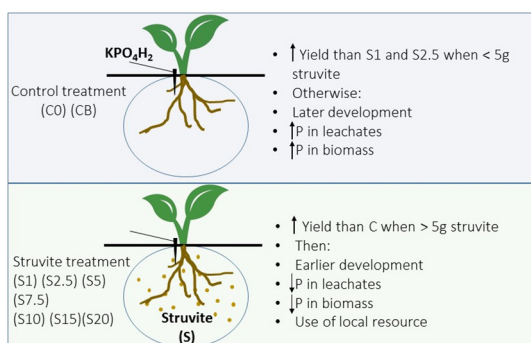
ARTICLE INFO

ABSTRACT

Urban agriculture (UA) is a means for cities to become more resilient in terms of food sovereignty while shortening the distance between production and consumption. However, intensive soilless UA still depends on the use of fertilizers, which relies on depleting non-renewable resources such as phosphorous (P) and causes both local and global impact for its production and application. With the aim to reduce such impacts and encourage a more efficient use of nutrients, this study assesses the feasibility of using struvite precipitated from an urban wastewater treatment plant as the unique source of P fertilizer. To do so, we apply various quantities of struvite (ranging from 1 to 20 g/plant) to the substrate of a hydroponic *Phaseolus vulgaris* crop and determine the yield, water flows and P balances. The results show that treatments with more than 5 g of struvite per plant produced a higher yield (maximum of 181.41 g/plant) than the control (134.6 g/plant) with mineral fertilizer (KPO$_4$H$_2$). On the other hand, P concentration in all plant organs was always lower when using struvite than when using chemical fertilizer. Finally, the fact that different amounts of struvite remained undissolved in all treatments denotes the importance to balance between a correct P supply to the plant and a decrease of P lost through the leachates, based on the amount of struvite and the irrigated water. The findings of this study show that it is feasible for UA to efficiently use locally recovered nutrients such as P to produce local food.

* Corresponding author at: Department of Chemical, Biological and Environmental Engineering, Universitat Autònoma de Barcelona (UAB), Campus UAB, 08193 Bellaterra, Barcelona, Spain.
 E-mail address: xavier.gabarrell@uab.cat (X. Gabarrell).
[1] These authors contributed equally to this research.

1. Introduction

Meeting the food demand of the ever-growing urban population is a global challenge. Since food provision to cities is highly dependent on long and complex supply chains, the distance between production and consumption points has extensively increased. This prevents nutrient recycling, while emitting huge amounts of greenhouse gases due to long-distance transport (Rees and Wackernagel, 1996; Thomaier et al., 2015). In this sense, moving towards more sustainable food systems should be a priority in the following years (European Commission, 2020). To do so, alternatives that narrow the distance between production and consumption points have already been reported, being urban agriculture one of the most prominent (Deelstra, 1987). However, this implies that the resources required to produce food, mainly fertilizers and water, must now be imported to cities. In the case of water, the use of rainwater harvesting systems combined with hydroponics can help meet the irrigation requirements without compromising the yield (Astee and Kishnani, 2010; Rufí-Salís et al., 2020b). On the other hand, the use of local fertilizers is still very limited, and often reduced to the use of compost (Thomaier et al., 2015). The vertical and soilless production systems have been reported to maintain greater yields while at the same time avoiding land occupation making it a viable alternative while in some cases environmentally better than open field production (Romeo et al., 2018). On the other hand the extensive use of mineral and synthetic fertilizers is necessary, causing potential and additional environmental damage in urban ecosystems if UA continues growing without the search for alternative fertilization methods (Sanjuan-Delmás et al., 2018; Rufí-Salís et al., 2020c; Kwon et al., 2021).

The case of phosphorus (P) fertilizers is of great relevance, since P is primarily obtained from non-renewable phosphate rocks. Moreover, previous studies quantify that 80% of the available stock of phosphate rocks is being used in the production of fertilizers (Shu et al., 2006). Since half of the world's current economic phosphate resources will have been used up by the end of the 21st century (Steen, 1998; Cordell et al., 2009) the European Union recognizes P as a critical resource (European Comission, 2014). Among its recommendations, a planned amendment of the fertilizer regulation encourages P recovery from local sources by enforcing a shift towards a more circular use of nutrients (European Comission, 2016).

In this sense, urban wastewater treatment plants (WWTPs) are well-known sources of secondary P. WWTPs have already been addressed as a potential alternative to importing mineral fertilizers (e.g. de-Bashan and Bashan, 2004; Kern et al., 2008; Shu et al., 2006). Struvite, also known as magnesium ammonium phosphate (MAP with the formula $NH_4MgPO_4 \cdot 6H_2O$) is a crystalline precipitate that has been gaining popularity as a way to recover P from wastewater. To induce its precipitation a molar ratio of 1:1:1 for magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphate (PO_4^{3-}) is needed, under specific pH conditions (8.5–9.5) (Buchanan et al., 1994; Bouropoulos and Koutsoukos, 2000; Le Corre et al., 2009). Originally the precipitation of struvite was associated to a major concern in WWTP being the cause of equipment damaging causing labor and infrastructure costs (Borgerding, 1972; Doyle et al., 2003; Stratful et al., 2004). Struvite forced precipitation has gained attraction since the 90's, not only to avoid infrastructure damage but also as a P recovery technique (Doyle et al., 2003). This process has been studied and improved in the past years making it a more efficient precipitation process (Le Corre et al., 2009; Sena and Hicks, 2018; Li et al., 2019). Although the production of struvite is gaining popularity, its commercial production is still scarce. The potential of P delivery of a WWTP in the form of struvite in the system where this study is located has been previously quantified by Rufí-Salís et al. (2020a), demonstrating the potential of these widespread installations to provide this ill distributed resource.

In terms of application, the properties of struvite as an effective source of nutrients ($P-PO_4^{3-}$, $N-NH_4^+$ and $Mg-Mg^{2+}$) for plants (Li and Zhao, 2003) and its low solubility in water (0.018 g·100 mL^{-1} at 25 °C) (Bridger et al., 1961) make it a slow-releasing valuable fertilizer that can reduce economic costs in agriculture (Rahman et al., 2014). However, only limited literature has explored the application of struvite in agricultural facilities. For example, Antonini et al. (2012), Uysal et al. (2014), Gell et al. (2011) and Liu et al. (2011) assessed the maize performance of struvite with different characteristics and origins in different soils. In a review made by Li et al. (2019) we can see that almost all struvite trials found that vegetables grown with struvite had the same -or even improved- performance compared to controls with conventional fertilizers.

Creating a closed-loop, waste-to-resource system such as that of struvite recovery within the city limits and not applying it at this scale seems contradictory within the concept of urban metabolism. In this sense, the synergy between struvite precipitation in urban WWTPs and urban agriculture seems worth exploring considering the potential of the latter to blur the lines between waste and resource within urban areas (Smit and Nasr, 1992; Ferreira et al., 2018; Rufí-Salís et al., 2020a). This article aims to assess the potential of struvite precipitated in a WWTP as a fertilizer within the framework of urban metabolism. Based on experimental and analytical results performed on a *Phaseolus vulgaris* crop grown in a hydroponic rooftop greenhouse, we determine the implications of fertilization with struvite in terms of yield, water flows and P balances and provide recommendations to further improve the performance of this waste-to-resource fertilizer.

2. Methodology

2.1. Characterization of the system

The present study was conducted in a rooftop greenhouse on the ICTA-ICP building, located in the campus of the Universitat Autònoma de Barcelona, 15 km away from Barcelona. The building is equipped with a 900m^2 rainwater harvesting system that stores water in a 100m^3 tank. Most of this rainwater is used in the rooftop greenhouse (122.8m^2) to irrigate crops with a hydroponic system, i.e. mixing water with nutrients before providing the solution through a dripping system (2 L/h) to the perlite substrate bags (40 L capacity). The perlite substrate has a pH of 7, an electrical conductivity of 0.09 dS·m^{-1}, a granulometry of [0–6] mm and 4 plants can be planted in each bag.

2.2. Fertilization and experimental set-up

Struvite granules were obtained from Aarhusvand A/S company from Aarhus, Denmark. This company distributes fertilizer grade struvite under the name PhosphorCare™, recovered using the Phosphogreen™ technology (Suez, 2018; Chrispim et al., 2019; Hall et al., 2020; Muys et al., 2021). This technology is based on a fluidized bed reactor that creates the specific conditions to precipitate struvite through the addition of magnesium chloride, sodium hydroxide and air. The final struvite granules have a size range of 0.5–1.5 mm.

Common bean plant (*Phaseolus vulgaris* var. Pongo) was chosen as the crop for this study, planting nursery plants (approximately 10–14 days old). To apply the struvite to the plants, we considered different possibilities. Mixing it with the nutrient solution was discarded because the system could not benefit from the slow-release characteristics of struvite. Thus, we choose to directly apply the granules to the plant roots. Considering this option, we designed a system that consisted on mixing perlite with struvite inside a low-density polyethylene perforated bag with holes of no more than 1 mm diameter (Fig. SM1 in the Supplementary materials). At the same time, this system allows the interaction between struvite granules and roots and avoids the loss of undissolved struvite into the leachates due to draining through the perlite bag.

Two different experiments were carried out: the validation test and the determination test, both of them using double growing lines with 8 substrate bags each (Figs. SM2 and SM14 in the Supplementary

materials). The validation test served as a previous experimental set-up to determine if the proposed methodology was functional and correct possible influencing variables in the experiment, such as the use of the plastic bag to retain the struvite close to the plant rhizosphere or to scale the most suitable quantities of struvite for the determination test. On the other hand the determination test was designed with the previous experience of the validation test. For control treatments, the nutrient solution applied to the crops in milligrams per litre was KPO_4H_2 – 136, KNO_3 – 101, K_2SO_4 – 217.5, $Ca(NO_3)_2$ – 164, $CaCl_2 \cdot H_2O$ – 111, $Mg(NO_3)_2$ – 148.3, Hortilon – 10, and Sequestrene – 10. In treatments with struvite, the mineral P source, KPO_4H_2 in this case, was excluded from the initial nutrient solution. All other mineral fertilizers were maintained.

2.3. Phosphorus balances

To account for the P balances, Eq. (1) was calculated on a plant basis for every control and struvite treatment. Fig. SM1 in the Supplementary material shows a diagram of the perforated bag with the elements displayed in Eq. (1).

$$P_{NS} + P_{SI} = P_{LV} + P_{ST} + P_{BN} + P_{SF} + P_{LIX} + P_{AC} \tag{1}$$

In Eq. (1), P represents mass of phosphorus. P_{NS} is the amount of mineral P supplied through the irrigation system during all the crop cycle. P_{SI} is the amount of P in the form of struvite applied at the beginning of the test. P_{LIX} is the amount of P in the leachates during all the crop cycle. P_{LV}, P_{ST}, and P_{BN}, represent P uptake by leaves, stem and beans, respectively. P_{SF} is the amount of remaining undissolved P in the form of struvite at the end of the test, plus the P adsorbed in the perlite granules. Finally, P_{AC} is the amount of dissolved P accumulated in the water retained in the substrate at the end of the crop. Three different biomass and substrate sampling dates were used in every test: 26, 54 and 78 days after planting (DAP) for the validation test and 23, 51 and 72 DAP for the determination test.

The initial nutrient concentration of the substrate was verified to be negligible at the beginning of the experiment through atomic spectroscopy and elemental analysis. Samples of the fertilizer solution were collected directly from the drippers placed in the perlite bags. Leachate samples were taken from plastic drainage buckets placed on one side of each line. To determine the P_{NS} and P_{LIX}, the respective samples were collected three times per week and externally analysed using ICP-OES atomic spectroscopy (Optima 4300DV by Perkin-Elmer). P_{SI} was quantified summing the amount of perlite in a specific bag with the amount of struvite that was applied, considering weights obtained by drying two struvite samples and two perlite samples at 105 °C in a furnace until reaching constant weight (reached after 3 days). P_{SF} was quantified differently in each test. In the validation test, all 4 samples for a specific treatment were homogenized after extracting the roots, using distilled water to separate the struvite granules from the roots. After this process, two random samples were dried at 105 °C in a furnace until reaching constant weight, then grounded and digested with concentrated HNO3 in a Single Reaction Chamber microwave and externally analysed using ICP-OES atomic spectroscopy. On the other hand, in the determination test, roots were shredded, homogenized and integrated within every individual substrate sample. Then, a fraction of these samples was dried and analysed using the same method as in the validation test.

P_{LV}, and P_{ST} were determined based on the nutrient content of every plant separately. Leaves and stem were separated, sorted into paper envelopes and dried in a furnace at 65 °C until reaching constant weight (reached after 7 days), grounded and digested with concentrated HNO3 in a Single Reaction Chamber microwave before analyzing externally the concentration of P through ICP-OES atomic spectroscopy. The same methodology was applied to determine the P_{BN}, with randomly chosen 500-gram bean samples being processed for every treatment.

The measured P content of beans was multiplied by the measured rates of biomass production to estimate the rate of P accumulation in crop biomass.

2.4. Validation test set-up and justification

From September 13th to December 3rd, 2018, 10 double growing lines were used (totalling 320 plants), distributing the treatments as showed in Fig. SM2 of the Supplementary material. The aim of this experiment was to validate and keep track of different parameters of the system, like for instance, make sure that the small, perforated bag did not have negative consequences on the crop development. To do so, we split the control lines into two different treatments, VCB and VC0, using standard nutrient solution with and without the bags, respectively. Secondly, to check the correct development of bean plants with struvite in a hydroponic system, we applied different struvite amounts per plant: 5, 10, 15, 20 and 25 g corresponding to the treatments tagged as V5, V10, V15, V20 and V25, respectively. Additionally, a treatment with no struvite was tagged as V0. These amounts of struvite were based on previous experiments done with the same crop species and variety in hydroponic cultivation that accounted for P uptake (Rufí-Salís et al., 2020c). One week after the first harvest, KPO_4H_2 was added in the nutrient solution of struvite treatments until the end of the harvest to ensure a good nutrition to the plants during the production period, which is highly demanding in P (e.g. Bender et al., 2015; Kouki et al., 2016; da Silva et al., 2019).

2.5. Validation test results

2.5.1. Production and phenological stages

The production results for the control treatments VCB and VC0 showed that the perforated bag did not have any effect on the correct crop development and yield (Figs. 1 and SM5), as the yields from the different lines do not differ between them (VC0_2 187.54 ± 69.35; VCB_1 186.15 ± 84.01 g/plant). Even though treatment VC0_1 generated more yield (224.84 ± 91.84 g/plant), it could be attributed to the fact that it was an exterior cropping line facing the border and thus received more radiation. Similarly, VCB_2 also produced more yield (195.45 ± 88.63 g/plant) than its replicate (VCB_1) although no significant differences where determined by the end of the experiment.

On the other hand, treatments with struvite (Figs. SM3 and SM4 of the Supplementary material) exerted a similar yield than the control treatments at the end of the crop. The treatment with the highest quantity of struvite (V25) had the highest production median (203.85 g/plant), while the treatment with the lowest quantity of struvite (V5) had the highest mean (216.15 ± 93.54 g/plant). On the other hand, the treatment without struvite produced a really low yield (7.19 ± 4.49 g/plant).

The similarities in terms of yield between all struvite treatments at the end of the cycle may be related to the addition of KPO_4H_2 fertilizer during the production phase. Moreover, we can see that struvite treatments produced more than the control in the first 3 harvests (35, 39 and 42 DAP) (Fig. SM6 in the Supplementary material). This effect is similarly observed for the phenological stages (Figs. 2 and SM7 to SM10 in the Supplementary material). For the parameters that were quantified in different dates (number of leaves (Fig. 2), side shoots (Fig. SM7), open flowers (Fig. SM8) and floral buttons (Fig. SM9)), we can see that the treatments with struvite not only had a correct early stage development, but also develop plant organs earlier than in control treatments.

2.5.2. Water

We applied more water in struvite treatments (125 L/plant) than to the control (94.76 L/plant) to ensure a proper dissolution of this fertilizer (Fig. SM11 – Supplementary material). However, we can see in Fig. SM12 in the Supplementary material that if a greater amount of
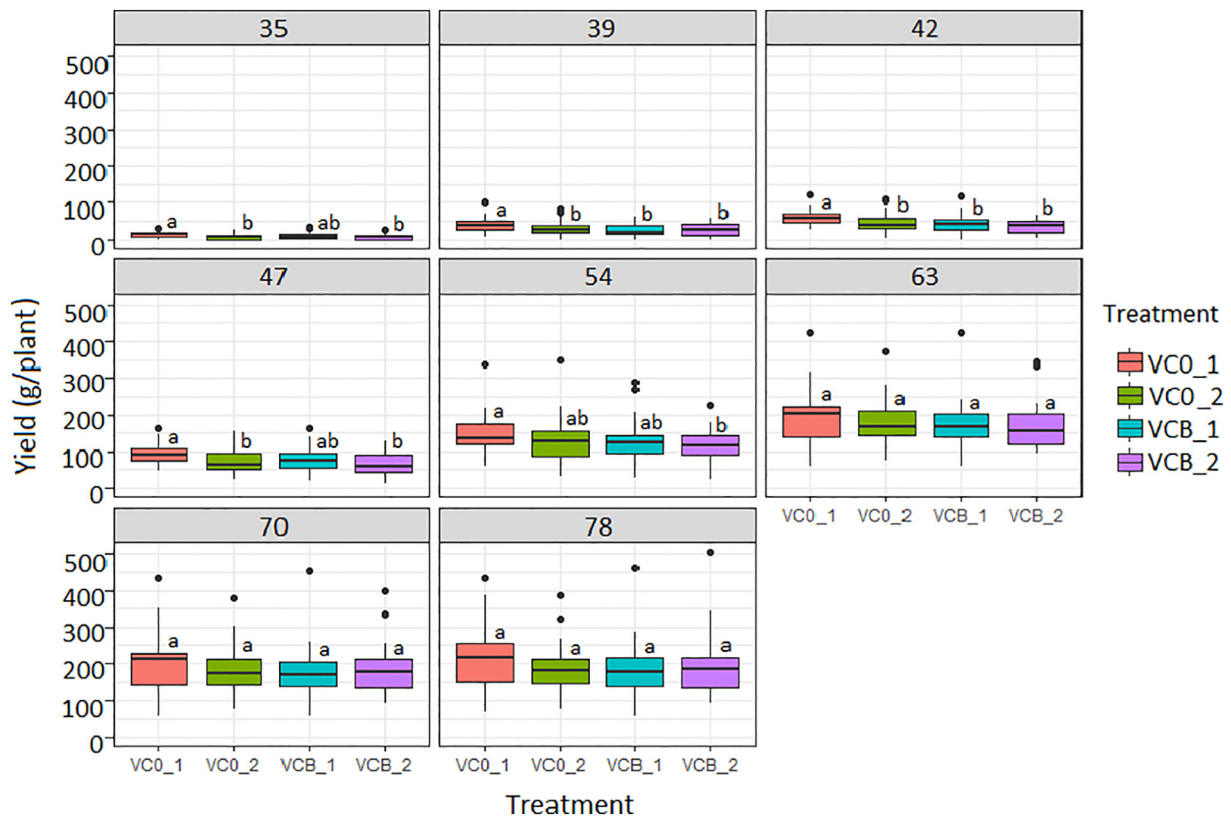
Fig. 1. Production (g/plant) of the control treatments in the validation test, with (VCB) and without (VC0) perforated bags for each harvest. Each panel in the figure grid represents the result for a harvesting day, with a total of 8 days (35 to 78 days after planting). Same letters (a,b) indicate no significant difference (p > 0.05) between treatment for each harvest time. Sample size for harvests 1, 2, 3, 4 and 5 (35- 54 DAP) corresponds to n = 28 plants, for harvests 6, 7 and 8 (63–78 DAP) n = 24 plants per treatment.
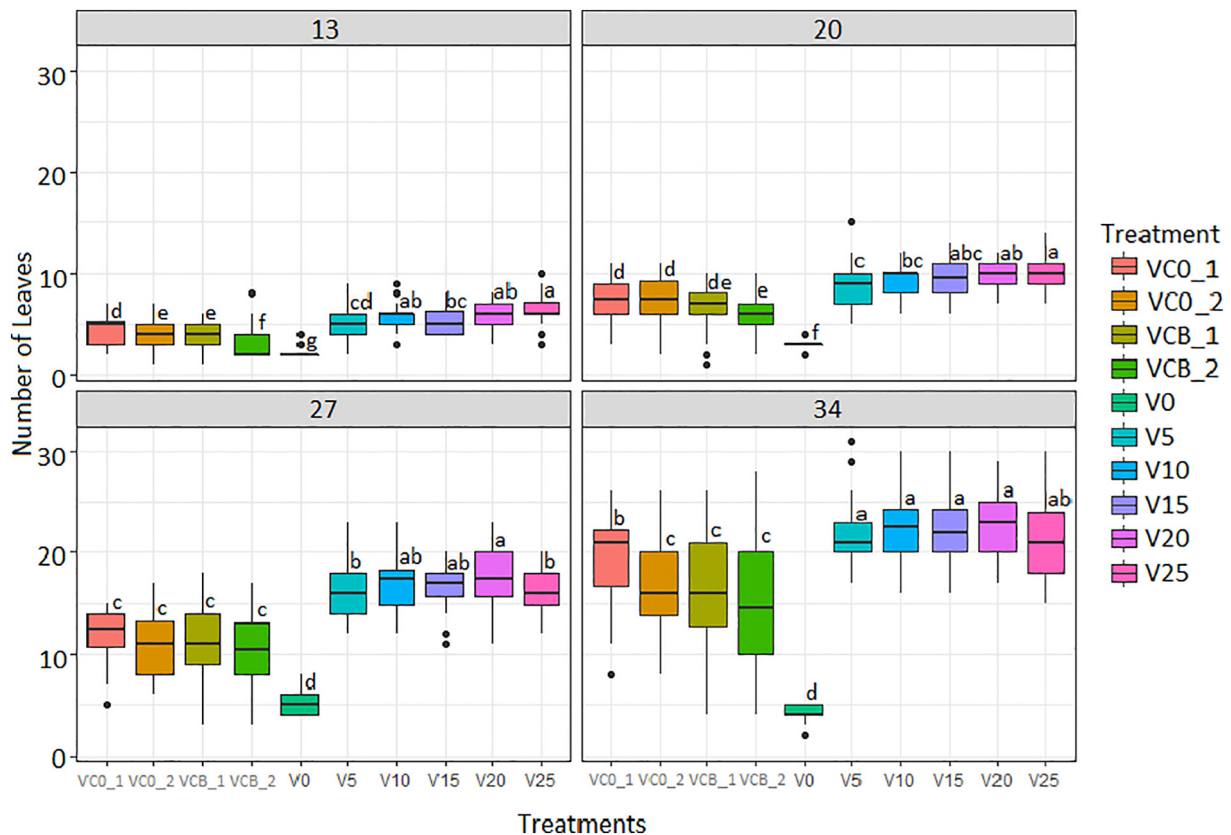
Fig. 2. Number of leaves per plant per treatment and Days after Transplanting (DAP) in the validation test (13, 20, 27, 34 DAP). Same letters (a, b, c, d, e, f, g) indicate no significant difference (p > 0.05) between treatment for each counting time. Sample size n = 32 for each treatment.

water flow through the perlite bag is provided through a greater irrigation, leachates emitted by the struvite treatments with higher concentrations (28.9 mg/L – V25) of this fertilizer tend to be similar to those of the control treatments. Obviously, this behaviour can only be observed before the irrigation with mineral P added during the harvesting process. Similarly, we can see that the perforated bag mechanism did not affect the P concentration in the leachates between the control treatment C0 and CB.

2.5.3. Phosphorus content

Fig. SM13 of the Supplementary material shows the total P content in the different plant organs as well as the content in the substrate, described as "undissolved". P content in the stem show low variability along all treatments, with V25 having the highest (0.083 ± 0.020 g P) and V0 the lowest (0.008 ± 0.002 g P) at the end of the crop cycle. A great P accumulation was observed in the low production of the V0 treatment with a content of 0.107 ± 0.005 g P (54 DAP) in beans, which was even higher than the highest observed in the control for VC0 (0.094 ± 0.013 g P –54 DAP), although the greater content was found for treatment V25 with 0.172 ± 0.023 g P (54 DAP). The V0 treatment doesn't show P results in leaves for 54 and 78 DAP because no leaves remained in the plant at the sampling time. For this same reason, there is a lack of data in beans for 78 DAP. Finally, concentration in beans for struvite treatments was similar to the one observed in the control. For all plant organs, a pattern in the accumulation of P in the plant tissue can be observed. In the first sampling all treatments show a rather low accumulation with greater content for plants with greater struvite quantities, in some cases also for the control treatments. For the second sampling, a bigger content difference can be seen with an acute increase of the V25 P content, especially for the stems and leaves. Finally, at 78 DAT, these differences between treatments even out and only treatment V0 remains significantly reduced. This last part however, does not correspond to the undissolved P in the perlite, where the P content in the substrate directly responds to the amount of struvite given, being always higher for the V25. The control treatments receive the P through irrigation making the existing content in the substrate comparably small.

2.6. Determination test set-up

From September 16th to November 27th, 2019, 8 double growing lines were used (totalling 256 plants), distributing the treatments as showed in Fig. SM14 of the Supplementary material. The determination test was designed based on the results of the validation test. The treatment distribution was randomized throughout the Greenhouse avoiding the influence of climatic conditions. Thus, the struvite treatments were recalculated, applying per plant: 1, 2.5, 5, 7.5, 10, 15 and 20 g corresponding to the treatments tagged as S1, S2.5, S5, S7.5, S10, S15 and S20, respectively. Struvite amounts below 5 g were applied based on the yield and P content performance in the validation test for V5. Since we found that the perforated bag did not affect plant development, we only used one control treatment, tagged as CB, which used the same perforated bag as the struvite treatments. Moreover, considering the yield and phenological findings in the validation test, we decided not to apply mineral P fertilizer to the struvite treatments at any point, so that struvite is the only source of P to the plants.

2.7. Statistical analysis

The analysed data were tested for normality using the Shapiro-Wilk test p > 0.05. Further on, the Levene's test p > 0.05 was used to determine homogeneity of variance. Once these parameters were validated the Duncan's multiple range test was used to assess the statistical significance of treatments. On the other hand, non-parametric data were analysed for significance using the Kruskal-Wallis test. The significance

between the treatments was marked with different letters in each plot. All statistical analyses were made with the R studio software.

3. Results

3.1. Yield

Figs. 3 (and SM15 and SM16 in the Supplementary material for the final total yield) shows the results of the accumulated yield per number of harvests, being the sixth harvest (71 DAP) the final one before uprooting the plants. Only treatments S1 (78.9 g/plant) and S2.5 (128.1 g/plant) had lower yields than the control treatment (134.6 g/plant), the first being significantly lower. On the other hand, all other treatments with 5 g of struvite or above produced more than the control treatment, demonstrating the potential of struvite to produce similar or even higher yields than with mineral fertilizer, as reported by Li et al. (2019).

As we can see in Fig. 3, it was not until the second harvest (42 DAP) that great differences were observed between the S1 yield and the other struvite treatments, while a decrease in S2.5 yield was observed between the 4th and 5th harvest, 57 and 64 DAP, respectively. Regarding the control treatment, the first harvest produced lower yield (6.31 ± 5.71 g/plant) than the S5 (14.97 ± 11.91) struvite treatment being even similar to the treatments with the lowest struvite application S1 (9.98 ± 8.51 g/plant).

This fact reinforces the idea that the application of struvite could be beneficial for early stage plant development, as the validation test showed better behaviour in struvite than in control in phenological variables. This fact could be related to the NH_4^+ supply by struvite, which could benefit the plant root balance when combined with nitrate supply (Marschner, 1995). The fact that previous literature suggests that NH_4^+ supply to common bean could be harmful for plant development (Chaillou et al., 1986; Guo et al., 2007) could be related to the amount of NH_4^+ supplied. Because struvite does not only enable a slow release of P but also of NH_4^+, reaching NH_4^+ accumulation to harmful levels seems improbable.

In terms of distribution, yields show an asymptote behaviour among treatments, where S20 produces the highest yield (g/plant) (181.41 ± 66.16) and S1, the lowest (78.94 ± 34.23). Fig. SM15 in the Supplementary material shows how treatment S10 was detected as the exception for this tendency in terms of mean production (150.50 ± 56.10), probably related to bias parameters like shapes in the greenhouse or a non-homogenic distribution of struvite in the perlite bag. However, boxplots represented in Fig. SM16 shows how the median of the final amount of yield harvested for S10 (155.70) follows the tendency, while not presenting outliers in the distribution.

3.2. Water

Fig. SM17 of the Supplementary materials shows that the irrigated water in the control and the struvite treatments was the same (42.5 L per plant), while Fig. 4 shows the accumulated P during the entire cycle in the different water streams. The quantity of P present in the control streams is much bigger than the one in the struvite streams, with the former irrigating and leaching 2.07 and 1.41 g of P per plant for the entire crop cycle, respectively. The fact that the P leachates are one order of magnitude smaller when using struvite (maximum of 0.03 g of P per plant in S20) could be related to the slow-release characteristic of struvite reported in the literature. A clear benefit of this finding is a decrease in both P depletion and freshwater eutrophication related to the leachates flow. Moreover, if the leachates of struvite treatments do not contain a large amount of P, it means that most of the struvite has been whether taken up by the plant or remains undissolved in the substrate.

When comparing Figs. SM12 and SM18 of the Supplementary material, we can see that P release by struvite is highly dependent on
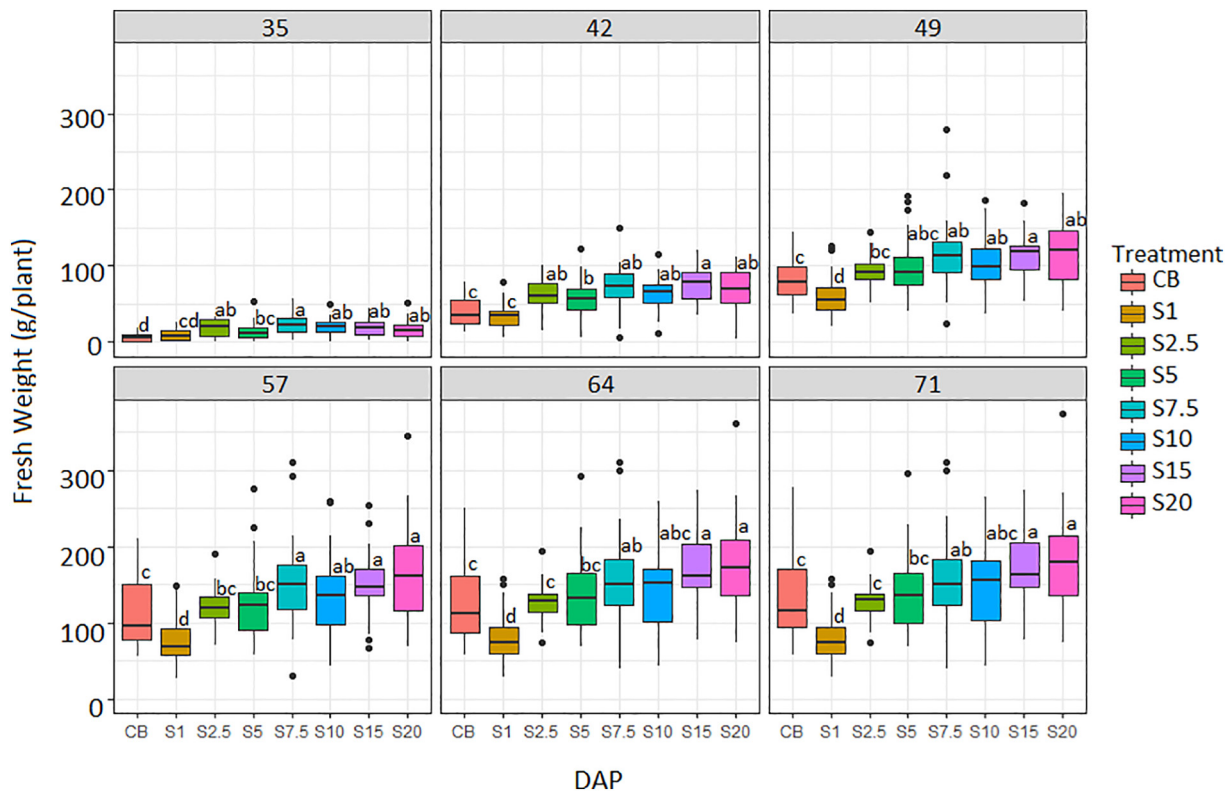
Fig. 3. Comparison of accumulated production of fresh bean per plant (g/plant) per treatment for each harvest time. Each panel in the figure grid represents the result for a harvesting day, with a total of 6 days (35 to 71 days after planting = DAP). Same letters (a, b, c, d) indicate no significant difference (p > 0.05) between treatment for each harvest time. Sample size for all harvests is n = 24 plants per treatment.

the input water flow, represented in Figs. SM11 and SM17 for the validation and determination test, respectively. Because the volume of irrigated water was three times less in the determination test (125.2 against 42.5 L per plant, respectively), the P observed in the leachates is less than in the validation test, considering the period where P was not supplied through mineral fertilizer in the validation test.

Differences are observed within the struvite treatments in Fig. 4, highly dependent on the quantity of struvite that was applied at the beginning of the crop. Treatments S1 and S2.5 stopped emitting P in the leachates just 14 DAP, which could have triggered P deficiencies. On

the other hand, treatments S15 and S20 were the only struvite treatments that did not stop emitting P to the leachates flow.

3.3. Substrate and undissolved struvite

Fig. 5 shows the distribution of P among all possible input and outputs considered in the system. At the end of the crop cycle, the control treatment supplied more P (2.07 g of P per plant) than the treatment with the highest amount of struvite (S20 - 1.90 g of P per plant). Most of the P supplied in the control treatments is discharged (68%), while in the struvite treatments it still remains in the substrate.
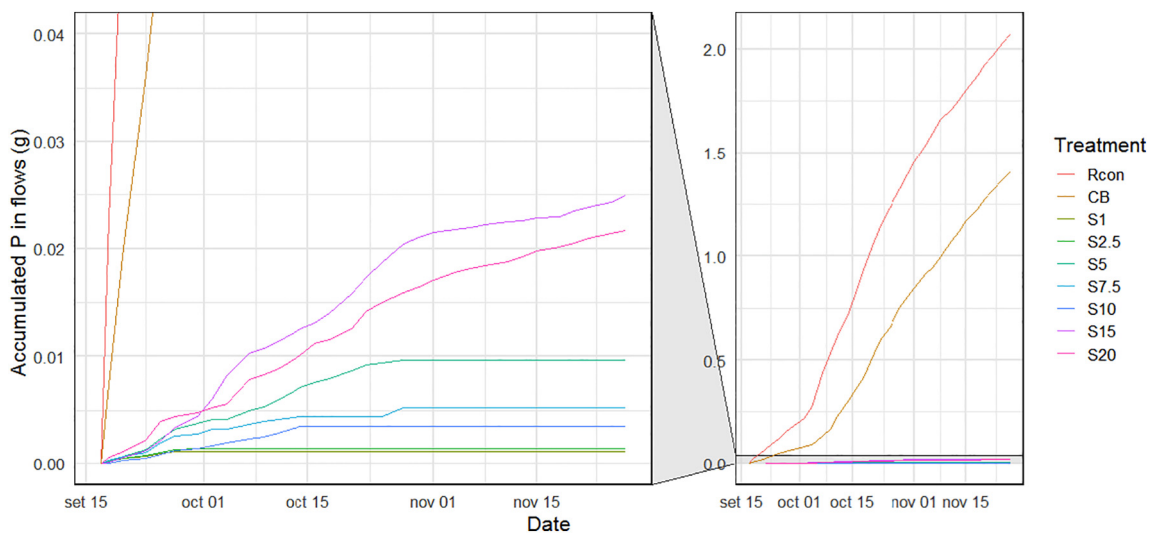

Fig. 4. Distribution of accumulated phosphorus in the irrigation and leachates of different treatments. Rcon: P in the control irrigation stream.

3.4. Biomass

In terms of biomass, we can see that the concentration of P (in g per kg) (Fig. 6) in all organs increases with the quantity of struvite applied to the treatment, having S15 and S20 similar concentrations in the leaves (7.0 ± 1.3 and 6.7 ± 1.8, respectively) and stem (5.0 ± 0.9 and 4.4 ± 1.2, respectively). However, the control treatment with mineral fertilizer presented higher concentrations of P than all struvite treatments, also in beans (7.3 ± 0.4). This is especially relevant in the case of beans, where the P deficiency in this organ directly affects the nutritional value of the product that is going to reach the market.

4. Discussion

Treatments S1 and S2.5 had lower yields than the control treatments, establishing a clear relationship between the yield and possible P deficiencies in these treatments. However, struvite remains undissolved in all treatments, even though the production and the distribution of P among plant organs was different between treatments (Figs. 3 and 6). The fact that we have undissolved struvite even in treatments S1 and S2.5 shows that the limitation is not only related to the quantity of struvite available, but also its dissolution (Figs. 4 and 6). While the struvite dissolution has been previously deemed to be due to the crystal granule size and placement (Talboys et al., 2016; Degryse et al., 2017) previous literature fails to report the effect of the irrigated water flow. Previous experiment on the struvite dissolution in deionized water make clear that a greater dissolution can be ensured with greater temperature and stirring energy as well as an acidic pH (Rahaman et al., 2006; Bhuiyan et al., 2007; Massey, 2007; Massey et al., 2009; Ariyanto et al., 2017) reaching greater dissolutions close to the commercial fertilizers. On the other hand the volume of water flows added to the crop has not been regarded as a determining factor when granulated struvite is directly added to the substrate, especially in hydroponic production. The obtained results in the present work shed light on the effect of the incoming irrigation on the struvite dissolution as well as loss of P in the leachate.

Because the volume of irrigated water was three times lower in the determination test, the P observed in the leachates is lower than in the validation test, considering the period where P was not supplied through mineral fertilizer. Moreover, there is a significant amount of P accumulated in the substrate bag at the end of the treatment in the control test. This stored P will be depleted if a successive crop is planted, since the small nursery plants will not benefit from all of it due to the lower needs of a smaller plant. With the addition of irrigation the accumulated nutrients in the perlite bag would eventually be moved to the leachates. By applying struvite (and verified by the small amount of P in the leachates in struvite treatments) this P is not stored and thus, not lost.

Based on the findings of this study, a well-designed struvite crop cycle needs to take into account two essential parameters. First, the quantity of struvite, considering that the quantity that remains undissolved at the end of the crop can be used again for a successive cycle. Second, the irrigation management, considering that if we modify this variable to increase the dissolution of struvite granules, we would also be increasing the P in the leachates. Moreover, since previous studies highlighted the effect of the surface area of the granules on the solubility of slow-release fertilizers (Chien and Menon, 1995; Gell et al., 2011; Li et al., 2019), the size used in our study (0.5–1.5 mm) seems adequate for the balance between P supply and P lost through the leachates. Literature with higher sizes reported solubility problems that affected early plant development (Talboys et al., 2016), while studies using lower sizes or powder do not report these problems (Gell et al., 2011; Antonini et al., 2012; Achat et al., 2014; Bonvin et al., 2015). Additionally, the use of nursery plants is preferable since the struvite low dissolution has been reported to be a disadvantage when providing P to feed the transition from seeds to nursery plants (Talboys et al., 2016).

Struvite supply per plant should always be above 5 g for *Phaseolus vulgaris*, considering that more quantity of struvite would release more P into the leachates, but ensure that P is available for plants. On the other hand, we should also account for the nutritional value of the beans, considering the ultimate function is to produce yield. In this sense, P in the biomass was a variable where the control treatment
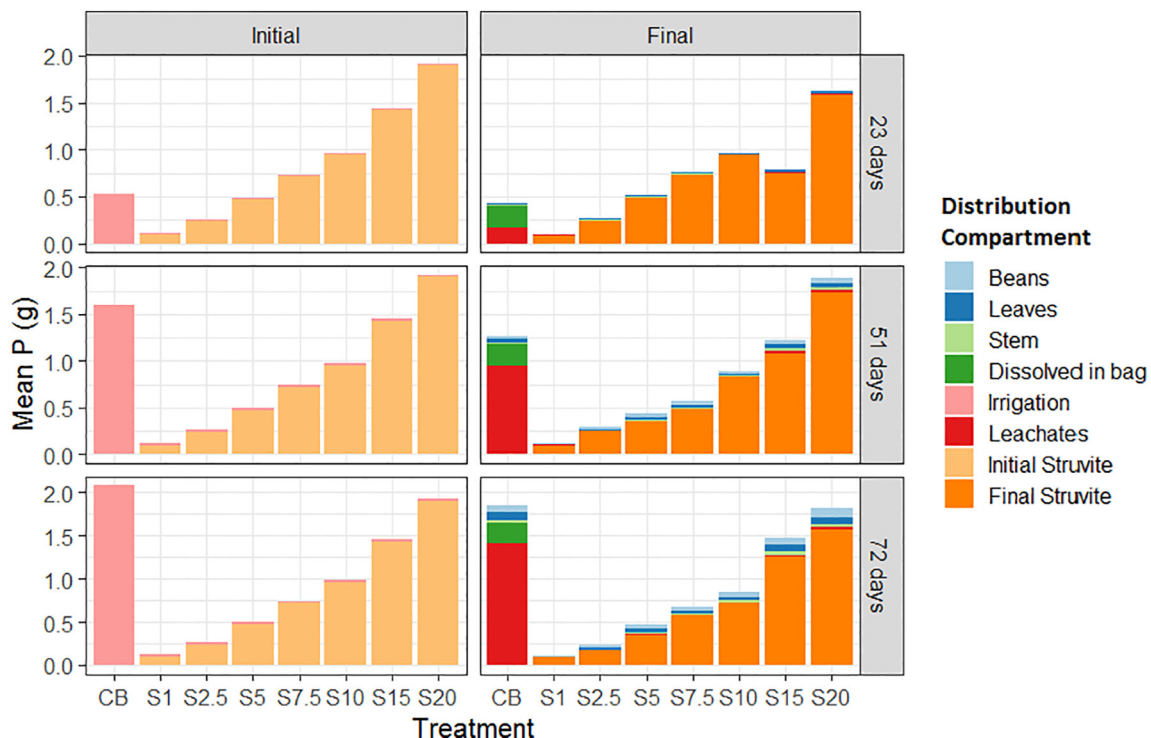

Fig. 5. P distribution among all water, biomass and substrate compartment flows. This amount of struvite at the end of the crop could be recovered, or the same substrate with struvite could be used for a successive crop.
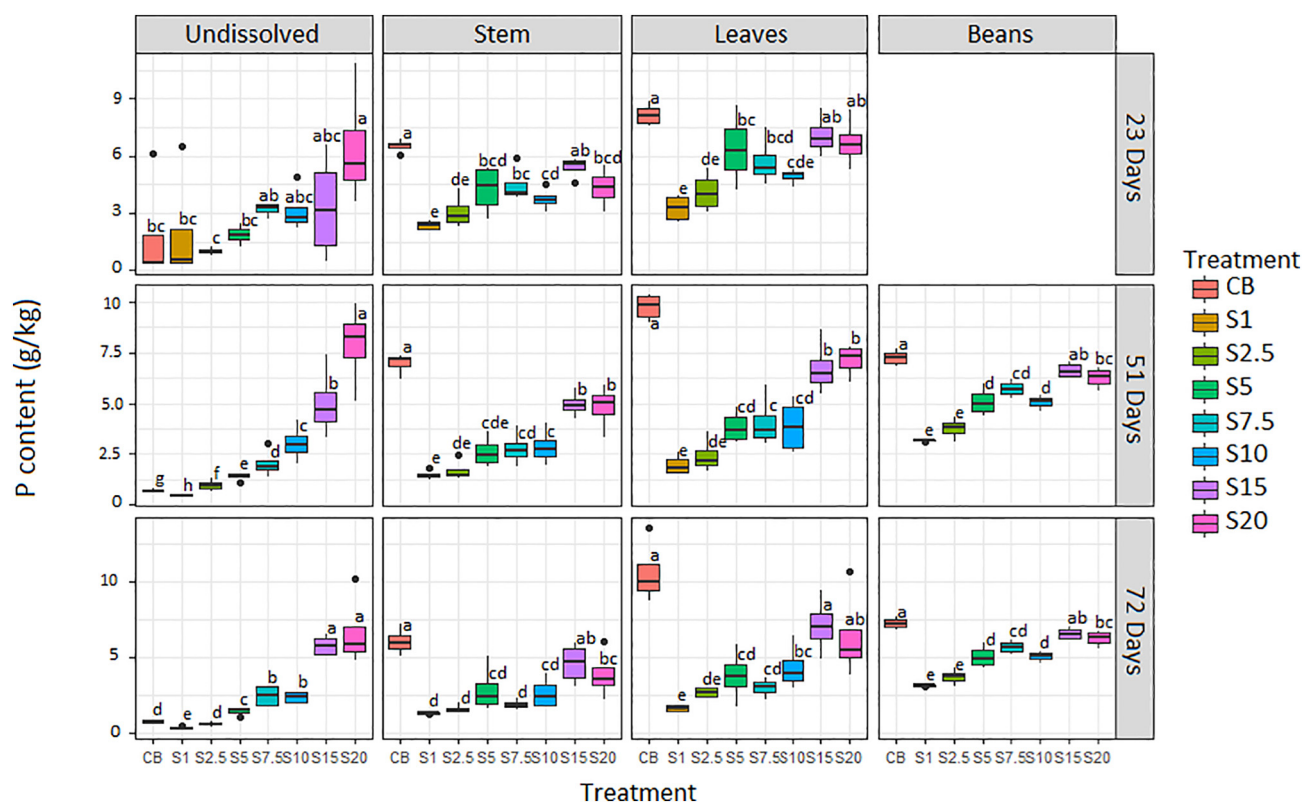
Fig. 6. Phosphorus concentrations (g/kg) in the different treatments, separated by plant organ and days after planting (DAP). Same letters (a, b, c, d, e, f, g, h) indicate no significant difference (p > 0.05) between treatment for each harvest time. Sample size for all organs n = 4. Undissolved P content n = 2.

had a better performance than struvite treatments. This uptake of similar P from struvite compared to soluble fertilizers has been previously reported by Ahmed et al. (2018) determining that different crops have a greater uptake of P while other have comparable or even lower growth. While *Phaseolus vulgaris* was not previously observed, a study with soybean was performed compared to the P uptake with triple superphosphate (TSP). The resulting crops show a similar uptake of both P sources by the plant with different quantities of P applied (Thompson, 2013). The P uptake in *Phaseolus vulgaris* with the use of struvite compared to monopotassium phosphate can also be seen in previous literature (Arcas-Pilz et al., 2021) although this experiment also explores the use of rhizobium inoculation as substitute for the N fertilization, obtaining a general reduction of plant growth. It is also important to keep in mind that the quantity of applied struvite is 2 g and 5 g for the proposed treatments. Rech et al., 2018 also discusses the low solubility of struvite compared to TSP, also mentioning a greater uptake of P by soybean and wheat with struvite fertilization compared to the control treatment.

Only S15 and S20 reach a similar P amount to the control in all plant organs. For this reason, a quantity between 15 and 20 g of struvite, a responsible irrigation management and growing successive crops with the same substrate constitutes the best option to grow a well-designed struvite bean crop cycle.

Although the P uptake of the struvite fertilized treatments appears to be equal or rather smaller than the control treatment the production is greater for all treatment with more than 5 g of struvite. In the literary review proposed by Ahmed et al., 2018 the increase of biomass and yield by plants fertilized with struvite can be related to the simultaneous dissolution of Mg and NH_4^+. Although the uptake of P is reported in this study the Mg and NH_4^+ concentration in the plant was not analysed. The Mg uptake has been reported to be strongly correlated with the given Mg in the struvite and can be pointed out as a possible source reason for greater growth and production (Antonini et al., 2012; Ahmed et al., 2018; Rech et al., 2018).

5. Conclusions

On the way towards developing more circular economies in cities, the recovery of scarce resources that can be utilised within the urban boundaries will play an important role. This study assessed the performance of the potential application of struvite in hydroponic bean crops to diminish the need for external resources in urban agriculture. Three main conclusions could be drawn from this analysis.

First, applying struvite in hydroponics crops equals and even increases the yield compared to mineral fertilizer while diminishing P losses in the leachates, contributing to both less nutrient depletion and eutrophication potential. In this sense, a quantity above 5 g/plant of struvite was observed to be enough for correct bean plant development and yield production.

Second, the input water flow was relevant in supplying enough P to the plants through dissolution using struvite. On the other hand, a correct water irrigation management is relevant to diminish P losses through overdissolution. Therefore, a balance between these two potential problems should be one of the key parameters when growing crops with struvite.

Third, a great quantity of struvite remains undissolved at the end of the crop in all treatments. In this sense, planting a successive cycle or recovering the struvite of the substrate could be alternatives to avoid losing valuable nutrients.

With the obtained information, it is adequate to say that the use of struvite in hydroponic production as a way to supply P is viable. Our study demonstrated that no special equipment or conditions were required for the use of struvite in hydroponic production. The use of this crystal therefore is strongly recommended and it extraction and use should be pursued for further optimization of the existing P sources.

Based on the findings presented in this paper, we believe that future research should focus on three different aspects. First, the role of NH_4^+

supplied by struvite on plant development during the first production phase. Second, the performance of crops if successive cycles are grown using the same undissolved struvite in hydroponic systems. Third and finally, the modelling of P release of struvite based on quantity applied and input water flow.

CRediT authorship contribution statement

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.149424.

References

Achat, D.L., et al., 2014. Plant-availability of phosphorus recycled from pig manures and dairy effluents as assessed by isotopic labeling techniques. Geoderma 232–234, 24–33. https://doi.org/10.1016/j.geoderma.2014.04.028.

Ahmed, N., et al., 2018. Struvite recovered from various types of wastewaters: characteristics, soil leaching behaviour, and plant growth. Land Degrad. Dev. 29 (9), 2864–2879. https://doi.org/10.1002/ldr.3010.

Antonini, S., et al., 2012. Greenhouse evaluation and environmental impact assessment of different urine-derived struvite fertilizers as phosphorus sources for plants. Chemosphere 89 (10), 1202–1210. https://doi.org/10.1016/j.chemosphere.2012.07.026 Elsevier Ltd.

Arcas-Pilz, V., et al., 2021. Improving the fertigation of soilless urban vertical agriculture through the combination of struvite and rhizobia inoculation in Phaseolus vulgaris. Front. Plant Sci. 12 (May), 1–13. https://doi.org/10.3389/fpls.2021.649304.

Ariyanto, E., Ang, H.M., Sen, T.K., 2017. The influence of various process parameters on dissolution kinetics and mechanism of struvite seed crystals. J. Inst. Eng. (India) Ser. A 98 (3), 293–302. https://doi.org/10.1007/s40030-017-0212-4 Springer India.

Astee, L.Y., Kishnani, N.T., 2010. Building integrated agriculture: utilising rooftops for sustainable food crop cultivation in Singapore. J. Green Build. 5 (2), 105–113. https://doi.org/10.3992/jgb.5.2.105 Allen Press.

Bender, R.R., Haegele, J.W., Below, F.E., 2015. Nutrient uptake, partitioning, and remobilization in modern soybean varieties. Agron. J. 107 (2), 563–573. https://doi.org/10.2134/agronj14.0435.

Bhuiyan, M.I.H., Mavinic, D.S., Beckie, R.D., 2007. A solubility and thermodynamic study of struvite. Environ. Technol. 28 (9), 1015–1026. https://doi.org/10.1080/09593332808618857.

Bonvin, C., et al., 2015. Plant uptake of phosphorus and nitrogen recycled from synthetic source-separated urine. Ambio 44 (2), 217–227. https://doi.org/10.1007/s13280-014-0616-6.

Borgerding, J., 1972. Phosphate deposits in digestion systems. J. Water Pollut. Control Fed. 44 (5), 813–819.

Bouropoulos, N.C., Koutsoukos, P.G., 2000. Spontaneous precipitation of struvite from aqueous solutions. J. Cryst. Growth 213 (3–4), 381–388. https://doi.org/10.1016/S0022-0248(00)00351-1 North-Holland.

Bridger, G.L., Salutsky, M.L., Starostka, R.W., 1961. Metal ammonium phosphates as fertilizers. 140th Meeting of the American Chemical Society, pp. 1–19.

Chaillou, S., et al., 1986. Nitrate or ammonium nutrition in french bean. Plant Soil 91, 363–365.

Chien, S.H., Menon, R.G., 1995. Factors affecting the agronomic effectiveness of phosphate rock for direct application. Fertil. Res. 41 (3), 227–234. https://doi.org/10.1007/BF00748312 Springer.

Chrispim, M.C., Scholz, M., Nolasco, M.A., 2019. Phosphorus recovery from municipal wastewater treatment: critical review of challenges and opportunities for developing countries. J. Environ. Manag. 248 (February), 109268. https://doi.org/10.1016/j.jenvman.2019.109268 Elsevier.

Cordell, D., Drangert, J.O., White, S., 2009. The story of phosphorus: global food security and food for thought. Glob. Environ. Chang. 19 (2), 292–305. https://doi.org/10.1016/j.gloenvcha.2008.10.009.

Le Corre, K.S., 2009. Phosphorus recovery from wastewater by struvite crystallization: a review. Crit. Rev. Environ. Sci. Technol. https://doi.org/10.1080/10643380701640573 Taylor & Francis Group.

De-Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). Water Res. https://doi.org/10.1016/j.watres.2004.07.014.

Deelstra, T., 1987. Urban agriculture and the metabolism of cities. Food Nutr. Bull. 9 (2), 1–3. https://doi.org/10.1177/156482658700900210.

Degryse, F., et al., 2017. Dissolution rate and agronomic effectiveness of struvite fertilizers – effect of soil pH, granulation and base excess. Plant Soil. Plant Soil 410 (1–2), 139–152. https://doi.org/10.1007/s11104-016-2990-2.

Doyle, J.D., et al., 2003. Chemical control of struvite precipitation. J. Environ. Eng. 129 (5), 419–426. https://doi.org/10.1061/(ASCE)0733-9372(2003)129:5(419).

European Comission, 2014. Critical raw materials. Internal Market, Industry, Entrepreneurship and SMEs.

European Comission, 2016. Paket zur Kreislaufwirtschaft. Verordnung des Europäischen Parlaments und des Rates mit Vorschriften für die Bereitstellung von Düngeprodukten mit CE-Kennzeichnung auf dem Markt und zur Änderung der Verordnungen. 0084, p. 1069.

European Commission, 2020. A Farm to Fork Strategy for a Fair, Healthy and Environmentally-friendly Food System, pp. 1–13 (February 2019).

Ferreira, A.J.D., 2018. Urban agriculture, a tool towards more resilient urban communities? Curr. Opin. Environ. Sci. Health 5, 93–97. https://doi.org/10.1016/J.COESH.2018.06.004 Elsevier.

Gell, K., et al., 2011. Safety and effectiveness of struvite from black water and urine as a phosphorus fertilizer. J. Agric. Sci. 3 (3), p67. https://doi.org/10.5539/jas.v3n3p67.

Guo, S., et al., 2007. Relationship between water and nitrogen uptake in nitrate- and ammonium-supplied Phaseolus vulgaris L. plants. J. Plant Nutr. Soil Sci. 170 (1), 73–80. https://doi.org/10.1002/jpln.200625073.

Hall, R.L., 2020. Phosphorus speciation and fertiliser performance characteristics: a comparison of waste recovered struvites from global sources. Elsevier. Geoderma 362, 114096. https://doi.org/10.1016/j.geoderma.2019.114096 (August 2019).

Buchanan, J.R., Mote, C.R., Robinson, R.B., 1994. Thermodynamics of struvite formation. Trans. ASAE Am. Soc. Agric. Biol. Eng. 37 (2), 617–621. https://doi.org/10.13031/2013.28121.

Kern, J., et al., 2008. Recycling and assessment of struvite phosphorus from sewage sludge. Agric. Eng. Int. CIGR J. 10 (December), 13.

Kouki, S., 2016. Phosphorus Fertilization Effect on Common Bean (Phaseolus vulgaris L .) -rhizobia Symbiosis. 25(1), pp. 1130–1137.

Kwon, M.J., 2021. Waste nutrient solutions from full-scale open hydroponic cultivation: dynamics of effluent quality and removal of nitrogen and phosphorus using a pilot-scale sequencing batch reactor. Elsevier Ltd. J. Environ. Manag. 281, 111893. https://doi.org/10.1016/j.jenvman.2020.111893 (December 2020).

Li, B., 2019. Phosphorous recovery through struvite crystallization: challenges for future design. Sci. Total Environ. 648, 1244–1256. https://doi.org/10.1016/j.scitotenv.2018.07.166 Elsevier B.V.

Li, X., Zhao, Q.L., 2003. Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer. Ecol. Eng. 20 (2), 171–181. https://doi.org/10.1016/S0925-8574(03)00012-0 Elsevier.

Liu, Y., et al., 2011. Eco-friendly production of maize using struvite recovered from swine wastewater as a sustainable fertilizer source. Asian Australas. J. Anim. Sci. 24 (12), 1699–1705. https://doi.org/10.5713/ajas.2011.11107.

Marschner, H., 1995. Mineral Nutrition of Higher Plants. 1. Academic P, San Diego, p. 889. https://doi.org/10.1006/anbo.1996.0155.

Massey, M.S., 2007. Struvite production from dairy wastewater and its potential as a fertilizer for organic production in calcareous soils. ASABE - Proceedings of the International Symposium on Air Quality and Waste Management for Agriculture https://doi.org/10.13031/2013.23823.

Massey, M.S., et al., 2009. Effectiveness of recovered magnesium phosphates as fertilizers in neutral and slightly alkaline soils. Agron. J. https://doi.org/10.2134/agronj2008.0144.

Muys, M., 2021. A systematic comparison of commercially produced struvite: quantities, qualities and soil-maize phosphorus availability. Sci. Total Environ. 756, 143726. https://doi.org/10.1016/j.scitotenv.2020.143726 The Authors.

Rahaman, M.S., et al., 2006. Exploring the determination of struvite solubility product from analytical results. Environ. Technol. 27 (9), 951–961. https://doi.org/10.1080/09593332708618707.

Rahman, M.M., 2014. Production of slow release crystal fertilizer from wastewaters through struvite crystallization - a review. Arab. J. Chem. 7 (1), 139–155. https://doi.org/10.1016/j.arabjc.2013.10.007 King Saud University.

Rech, I., et al., 2018. Solubility, diffusion and crop uptake of phosphorus in three different struvites. Sustainability (Switzerland) 11 (1). https://doi.org/10.3390/su11010134.

Rees, W., Wackernagel, M., 1996. Urban ecological footprints: why cities cannot be sustainable - and why they are a key to sustainability. Environ. Impact Assess. Rev. 16 (4–6), 223–248. https://doi.org/10.1016/S0195-9255(96)00022-4.

Romeo, D., Vea, E.B., Thomsen, M., 2018. Environmental impacts of urban hydroponics in Europe: a case study in Lyon. Procedia CIRP 69 (May), 540–545. https://doi.org/10.1016/j.procir.2017.11.048 The Author(s).

Rufí-Salís, M., Brunnhofer, N., et al., 2020. Can wastewater feed cities? Determining the feasibility and environmental burdens of struvite recovery and reuse for urban regions. Sci. Total Environ. 737, 139783. https://doi.org/10.1016/j.scitotenv.2020.139783 Elsevier B.V.

Rufí-Salís, M., Petit-Boix, A., Villalba, G., Ercilla-Montserrat, M., et al., 2020. 'Identifying eco-efficient year-round crop combinations for rooftop greenhouse agriculture', International Journal of Life Cycle Assessment. Int. J. Life Cycle Assess. https://doi.org/10.1007/s11367-019-01724-5.

Rufí-Salís, M., Petit-Boix, A., Villalba, G., Sanjuan-Delmás, D., et al., 2020. Recirculating water and nutrients in urban agriculture: an opportunity towards environmental sustainability and water use efficiency? J. Clean. Prod. 261, 121213. https://doi.org/10.1016/J.JCLEPRO.2020.121213 Elsevier.

Sanjuan-Delmás, D., et al., 2018. Environmental assessment of an integrated rooftop greenhouse for food production in cities. J. Clean. Prod. 177, 326–337. https://doi.org/10.1016/j.jclepro.2017.12.147.

Sena, M., Hicks, A., 2018. Life cycle assessment review of struvite precipitation in wastewater treatment. Resour. Conserv. Recycl. https://doi.org/10.1016/j.resconrec.2018.08.009.

Shu, L., et al., 2006. An economic evaluation of phosphorus recovery as struvite from digester supernatant. Bioresour. Technol. 97 (17), 2211–2216. https://doi.org/10.1016/J.BIORTECH.2005.11.005 Elsevier.

da Silva, D.A., et al., 2019. Analysis of the common bean (Phaseolus vulgaris L.) transcriptome regarding efficiency of phosphorus use. PLoS One 14 (1), 1–27. https://doi.org/10.1371/journal.pone.0210428.

Smit, J., Nasr, J., 1992. Urban agriculture for sustainable cities: using wastes and idle land and water bodies as resources. Environ. Urban. 4 (2), 141–152. https://doi.org/10.1177/095624789200400214 IIED3 Endsleigh Street, London WC1H ODD, United Kingdom.

Steen, I., 1998. Phosphorus availability in the 21st Century: management of a non-renewable resource. Phosphorus Potassium 25–31.

Stratful, I., Scrimshaw, M.D., Lester, J.N., 2004. Removal of struvite to prevent problems associated with its accumulation in wastewater treatment works. Water Environ. Res. 76 (5), 437–443. https://doi.org/10.2175/106143004X151491.

Suez, 2018. Recycle phosphorus from effluent to produce a valuable fertilizer-Phosphogreen.Available at:. https://www.suezwaterhandbook.com/degremont-R-technologies/sludge-treatment/recovery/recycle-phosphorus-from-effluent-to-produce-a-valuable-fertilizer-Phosphogreen (Accessed: 18 June 2021).

Talboys, P.J., et al., 2016. Struvite: a slow-release fertiliser for sustainable phosphorus management? Plant Soil 401 (1–2), 109–123. https://doi.org/10.1007/s11104-015-2747-3.

Thomaier, S., 2015. Farming in and on urban buildings: present practice and specific novelties of Zero-Acreage Farming (ZFarming). Renew. Agric. Food Syst. 30 (01), 43–54. https://doi.org/10.1017/S1742170514000143 Cambridge University Press.

L Thompson . (2013) 'Field evaluation of the availability for corn and soybean of phosphorus recovered as struvite from corn fiber processing for bioenergy', Graduate Theses and Dissertations. Available at: http://lib.dr.iastate.edu/etd/13173.

Uysal, A., et al., 2014. Optimization of struvite fertilizer formation from baker's yeast wastewater: growth and nutrition of maize and tomato plants. Environ. Sci. Pollut. Res. 21 (5), 3264–3274. https://doi.org/10.1007/s11356-013-2285-6.