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Plant availability of secondary P sources in growing media-based crop production

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Summary

Phosphorus (P) is an essential nutrient for plant growth. In plant production, a sufficient P supply for plants is commonly provided by fertilization with rock phosphate (RockP)-based fertilizers. However, the RockP resources are finite and the worldwide reserves are located in only a few countries. To address this issue of P scarcity, the use of secondary P sources in crop production based on growing media may help to conserve the finite resources and mitigate the limited geopolitical accessibility. However, there is a lack of knowledge concerning the plant availability of secondary source-P being suitable for soilless crop production. To investigate plant P availability of secondary P sources, pot trials were conducted using *Tagetes patula* x *erecta* as a P-sensitive model plant and white peat as growing medium. Fertilizer efficacy of secondary source-P was compared to that of a highly processed, water-soluble P-form derived from RockP (monocalcium phosphate (MCP)). In addition, common growing media analyses (CAT- and CAL-method) were tested for their suitability to reflect plant-available secondary source-P.

For the first evaluation, a screening trial with different secondary P sources (n = 17) derived from various P-recovery scenarios (five untreated feedstock, four thermally treated feedstocks, three thermochemically treated feedstocks and five precipitation products) was conducted at a growing medium pH tolerated by most horticultural crops (pH 6.0) (section I). Only three of the 17 tested secondary P sources (all precipitated struvite-forms) showed fertilizer efficacy comparable to MCP. The remaining sources showed a P uptake ranging from 4% to 91% of MCP-P. Precipitates from liquid waste streams and untreated organic wastes, with the exception of sewage sludge and compost, had a P uptake varying between 71% and 100%. The widest variability (4%–86%) was exhibited by thermally and thermochemically treated secondary P sources.

Beside the commonly used growing media pH of around 6, acidophilic plants such as *Azalea* species require a low growing medium pH. To investigate plant P availability of secondary P sources under acidic condition in the growing medium and to investigate the effect of contrasting pH levels (4.5, 6.0) in the growing medium on the availability of secondary source-P, three pot trials were conducted (section II). Among the trials, 11 secondary P sources (one untreated feedstock: biogas digest, eight thermally treated feedstocks: six sewage sludge ashes, two biochars, one thermochemically treated feedstock: cinder product, and one precipitation product: struvite) were tested and regarding their plant P

availability. As benchmark, MCP and finely ground RockP were used. At a pH of 6.0, the observed plant P uptake for each of the secondary P sources as percentage of the MCP value were as follows: 68% for the biogas digest, 19–25% for sewage sludge ashes, 2–54% for the biochars, 1–2% for the cinder product, 68–119% for the struvite, and 15–20% for the RockP. At pH of 4.5, the observed plant P uptakes as percentage of the MCP value the followings: 89% for the biogas digest, 63–83% for sewage sludge ashes, 5–69% for the biochars, 2–3% for the cinder product, 80–113% for the struvite, and 72–91% for the RockP. The exhibited enhancement of plant availability under acidic conditions in the growing medium differed between the secondary P sources, but was for products exhibiting a plant availability of practical relevance the highest for sewage sludge ashes.

In addition to the effect of contrasting pH in the growing medium on plant P availability, the effect of grain size was studied in two pot trials. Among the secondary P sources, four products (two thermally treated feedstocks: one sewage sludge ash, one biochar, one thermochemically treated feedstock: cinder product, and one precipitated struvite) exhibited coarser particles compared to the powder structure of others of the same type. Secondary P sources were tested as received and in finely ground powder form and their plant P availability was compared to that of MCP (section III). For all secondary P sources a higher plant P availability was observed when applied as powder. The observed plant P uptake as percentage of the MCP value for the secondary P sources when applied as received was: 4% for the sewage sludge ash, 1% for the biochar, 1–2% for the cinder product, and 63% for the struvite. For the applied powder form, observed values for plant P uptake as percentage of the MCP value were: 60% for the sewage sludge ash, 22% for the biochar, 2–13% for the cinder product, and 95% for the struvite.

According to the presented results, among the secondary P sources, precipitated struvite forms showed in most cases a similarly high plant P availability compared to water-soluble MCP. Hence, it can be concluded, that for plant production based on growing media, struvites are the most promising substitutes for highly processed P-fertilizers derived from the limited reserves of RockP. However, apart from a very few exceptions, the fertilization with other secondary P sources led to similar plant fresh weights, but just approximately half the plant P uptake as MCP. This indicates, that twice the amount of these secondary P sources seems to be suitable to obtain similar amounts of plant-available P at pH conditions in the growing medium tolerated by most horticultural crops (pH 6). However, for these secondary P sources, a higher plant P availability was observed under more acidic pH conditions (pH <5) in the growing medium that are suitable for cultivation of acidophilic plants. Here, the derived factor to obtain a similar amount of plant-available P compared to MCP is 1.3. To ensure the highest possible plant availability of each secondary P source, they should be admixed into the growing medium as finely ground powder, since a reduction in P availability can be expected for coarser grinds. To predict plant-available P in the growing medium, extraction methods (CAT and CAL-method) were performed at the beginning of the experiments and the extractable amounts of P were related to plant P uptake after plants had reached a marketable stage, which determined the end of the experiment. A close correlation between plant P uptake and P_{CAT} ($R^2 = 0.76$) and P_{CAL} ($R^2 = 0.78$), respectively, was observed (section I). However, an innovative approach combining CAT- and CAL-extractable amounts in the growing medium (P_{mod}) exhibits the best fit ($R^2 = 0.89$) for plant P uptake at the end of this experiment. This close relation to plant P uptake was further confirmed in other pot trials (section II: $R^2 = 0.83$, section III: $R^2 = 0.87$). However, P_{mod} could not reflect plant availability of iron (FeP) and aluminum phosphates (AlP) or secondary P sources, which presumably contain relevant proportions of these P compounds (e.g., sewage sludge ashes), under acidic conditions in the growing medium. Here, a strong underestimation of plant available P was shown for $P_{mod,}$ which is attributed to the solvents (CAT, CAL) inability to extract FeP or AlP. This implies the need for solvent modifications or the need of an additional solvent to satisfactorily characterize plant available secondary source-P by growing media analyses. To fully understand the P_{mod}'s ability to characterize plant available secondary source-P, an assessment including all experimental data (including earlier sampling times) and extractable P in the growing medium after harvests was considered (residuals P_{mod}). It was shown that, the amount of plant available P in the growing medium could be mapped in the same way regardless of the sampling time. Excluding the data for which a limitation of the prediction of plant available P could be proven, a very close correlation between P_{mod} at the beginning of the trial and the P uptake of the plant + the amount of P extractable in the growing medium at the end of the trial was found, when all trial data from section I-III were taken into account ($R^2 = 0.90$). Thus, P_{mod} seems to be a promising approach to characterize plant availability of secondary source-P in crop production using peat-based growing media and should be further validated in experiments with other crops, other secondary P sources and multi-component growing media.

Zusammenfassung

Phosphor (P) ist ein essenzielles Nährelement für das Pflanzenwachstum. Eine ausreichende P-Versorgung der Pflanzen wird in industriellen Produktionssystemen durch Düngung gewährleistet. Die hierzu eingesetzten P-Dünger bestehen in der Regel aus hoch aufgeschlossenem weicherdigem Rohphosphat (RockP). Die abbauwürdigen Reserven an RockP sind endlich und ihr Vorkommen beschränkt sich zudem nur auf wenige Länder weltweit. Um einer künftigen Knappheit von Düngemitteln auf Basis von Rohphosphat zu begegnen sowie die geopolitische Abhängigkeit zu mildern, könnte die Verwendung von P aus Reststoffströmen (sekundäre P-Quellen) in der bodenunabhängigen Pflanzenproduktion einen Beitrag leisten. Inwieweit sich solche sekundären P-Quellen hinsichtlich ihrer Düngewirkung für die Produktion von Pflanzen in Kultursubstraten eignen, ist fraglich. Ziel dieser Arbeit war es deshalb, die Pflanzenverfügbarkeit von sekundären P-Quellen zu untersuchen. Hierzu wurde in Experimenten *Tagetes patula* x *erecta* als P-sensitive Modellpflanze in Weißtorf kultiviert und die Düngewirkungen von sekundären P-Quellen mit einer voll aufgeschlossenen P-Form (Calciumdihydrogenphosphat (MCP)) verglichen. Darüber hinaus wurde geprüft, inwieweit sich etablierte Kultursubstratanalysen (CAT- und CAL-Methode) eignen, die Pflanzenverfügbarkeit von Sekundär-P zu charakterisieren.

Eine erste Bewertung erfolgte mittels eines Screeningversuches, in dem die Pflanzenverfügbarkeit von 17 sekundären P-Quellen aus unterschiedlichen Rückgewinnungsszenarien (fünf unbehandelte Ausgangsstoffe, vier thermisch behandelte Reststoffe, drei thermochemisch behandelte Reststoffe und fünf Fällungsprodukte) untersucht wurde (Sektion I). Für die Untersuchung wurde der pH-Wert im Kultursubstrat auf einen für Topfkulturen üblichen Wert von 6.0 eingestellt. Nur drei der 17 getesteten sekundären P-Quellen (alles gefällte Struvit-Formen) zeigten eine mit MCP vergleichbare Düngewirksamkeit. Bei den übrigen sekundären P-Quellen lag die P-Aufnahme zwischen 4 und 91 % des MCP-P. Fällungsprodukte aus flüssigen Abfallströmen und unbehandelten organischen Abfällen - mit Ausnahme von Klärschlamm und Kompost - wiesen eine P-Aufnahme zwischen 71 und 100 % der wasserlöslichen Kontrolle auf. Die größte Variabilität (4 – 86 %) wurde bei thermisch und thermochemisch behandelten sekundären P-Quellen beobachtet.

Neben dem in der Kultursubstrat-basierten Pflanzenproduktion üblicherweise verwendeten pH-Wert von etwa 6, benötigen acidophile Pflanzen wie beispielsweise Azaleenarten einen niedrigen pH-Wert. Um die Pflanzenverfügbarkeit sekundärer P-Quellen unter diesen deutlich saureren Bedingungen zu untersuchen und die Auswirkungen unterschiedlicher pH-Werte (4,5, 6,0) im Kultursubstrat auf die Verfügbarkeit sekundärer P-Quellen zu ermitteln, wurden drei Experimente durchgeführt (Sektion II). In diesen Experimenten wurden insgesamt 11 verschiedene sekundäre P-Quellen (ein unbehandelter Reststoff: Biogasgärrest, acht thermisch behandelte Reststoffe: sechs Klärschlammaschen und zwei Biokohlen, ein thermochemisch behandelter Reststoff: Schlackenprodukt, und ein Fällungsprodukt: Struvit) hinsichtlich ihrer Pflanzenverfügbarkeit geprüft. Als Referenz wurde MCP sowie ein fein gemahlenes RockP verwendet. Bei einem pH-Wert von 6,0 wurden die folgenden P-Aufnahmen in Prozent des MCP-Wertes beobachtet: 68 % für den Biogasgärrest, 19 – 25 % für die Klärschlammaschen, 2 – 54 % für die Biokohlen, 1 – 2 % für das Schlackenprodukt, 68 – 119 % für das Struvit und 15 – 20 % für das RockP. Bei einem pH-Wert von 4,5 betrugen die ermittelten P-Aufnahmen der Pflanze in Prozent des MCP-Wertes: 89 % für den Biogasgärrest, 63 – 83 % für die Klärschlammasche, 5 – 69 % für die Biokohlen, 2 – 3 % für das Schlackenprodukt, 80 – 113 % für das Struvit und 72 – 91% für das RockP. Die festgestellte Verbesserung der Pflanzenverfügbarkeit unter sauren Bedingungen im Kultursubstrat war bei den sekundären P-Quellen unterschiedlich stark. Für sekundäre P-Quellen, die eine praxisrelevante Pflanzenverfügbarkeit aufweisen (alle außer einer Biokohle und das Schlackenprodukt), war die Verbesserung der Verfügbarkeit für die Klärschlammasche am höchsten.

Neben dem Effekt des pH-Wertes auf die Pflanzenverfügbarkeit von sekundären P-Quellen wurde weiterhin der Einfluss der Körnungsgröße die in zwei Experimenten untersucht (Sektion III). Vier der untersuchten sekundären P-Quellen (zwei thermisch behandelte Ausgangsstoffe: eine Klärschlammasche und eine Biokohle, ein thermochemisch behandelter Ausgangsstoff: ein Schlackenprodukt, und ein gefälltes Struvit) wiesen im Vergleich zu anderen Produkten gleichen Typs eine wesentlich gröbere Struktur auf. Geprüft wurde die Pflanzenverfügbarkeit der sekundären P-Quellen im Anlieferungszustand und in fein gemahlener, pulverisierter Form. Als Vergleichswert diente das von den Pflanzen aufgenommene MCP-P. Für alle sekundären P-Quellen zeigte sich eine höhere P-Aufnahme der Pflanze, wenn fein vermahlenes Pulver gedüngt wurde. Die P-Aufnahme der Pflanzen als

Prozentsatz von MCP betrug für die sekundären P-Quellen bei Ausbringung im Anlieferungszustand: 4 % für die Klärschlammasche, 1 % für die Biokohle, 1 – 2 % für das Schlackenprodukt und 63 % für das Struvit. Die beobachteten Werte für die P-Aufnahme der Pflanze als Prozentsatz der MCP-Kontrolle, wenn fein vermahlenes Material appliziert wurde, betrugen: 60 % für die Klärschlammasche, 22 % für die Biokohle, 2 – 13 % für das Schlackenprodukt und 95 % für das Struvit.

Ausgehend von den dargestellten Ergebnissen zeigte sich in den meisten Fällen für gefällte Struvit-Formen eine mit dem wasserlöslichen MCP-P vergleichbar hohe Pflanzenverfügbarkeit. Folglich stellt eine Verwendung von Struvit in der Grunddüngung von Kultursubstraten die vielversprechendste Alternative für hoch verarbeitete Rohphosphate dar. Die Pflanzenverfügbarkeit der restlichen sekundären P-Quellen ist zwar geringer als die von Struvit, kann bis auf wenige Ausnahmen aber immer noch als relativ hoch bewertet werden. Durchschnittlich führte hier eine Düngung zu vergleichbaren Frischgewichten der Pflanzen wie eine MCP-Düngung, allerdings nur zu einer etwa halb so hohen aufgenommenen P-Menge. Dies deutet darauf hin, dass etwa die doppelte Menge dieser sekundären P-Quellen appliziert werden müsste, um eine vergleichbare Menge an pflanzenverfügbarem P wie von MCP-P unter pH-Bedingungen von 6 im Kultursubstrat zu erreichen. Unter deutlichen saureren Bedingungen im Kultursubstrat konnte eine deutlich höhere Pflanzenverfügbarkeit dieser sekundären P-Quellen nachgewiesen werden. Hier beträgt die notwendige Düngermenge zur Erzielung einer ähnlichen pflanzenverfügbaren P-Menge wie mit MCP etwa das 1,3-fache. Um eine möglichst hohe Pflanzenverfügbarkeit von sekundären P-Quellen zu gewährleisten, sollten sie als fein gemahlenes Pulver in das Kultursubstrat eingemischt werden, da bei Verwendung einer gröberen Vermahlung eine Verringerung der P-Verfügbarkeit zu erwarten ist.

Zur Überprüfung inwieweit sich die CAT- bzw. CAL-Methode eignet, pflanzenverfügbares P aus sekundären P-Quellen zu charakterisieren, wurde die zu Beginn des Screeningversuchs extrahierbare P-Menge (P_{CAT}, P_{CAL}) mit der P-Aufnahme der Pflanzen zu Versuchende korreliert. Ein enger Zusammenhang wurde zwischen der P-Aufnahme der Pflanzen und P_{CAT} (R^2 = 0,76) bzw. P_{CAL} (R_2 = 0,78) festgestellt. Durch eine innovative Kombination von P_{CAT} und P_{CAL} (P_{mod}) konnte die Beziehung zwischen dem vorhergesagten pflanzenverfügbaren P im Kultursubstrat und der P-Aufnahme der Pflanze weiter verbessert werden (R^2 = 0,89). Diese enge Beziehung zwischen P_{mod} und der P-Aufnahme der Pflanzen wurde in weiteren Experimenten bestätigt (Sektion II: $R^2 = 0{,}83$, Sektion III: $R^2 = 0{,}87$). P_{mod} konnte jedoch die Pflanzenverfügbarkeit von Eisen-(FeP) und Aluminiumphosphaten (AlP) bzw. von sekundären P-Quellen, in denen diese P-Verbindungen vermutlich abundant sind (z. B. Klärschlammasche), insbesondere unter sauren Bedingungen im Kultursubstrat nicht widerspiegeln. Hier wurde für P_{mod} eine starke Unterschätzung des pflanzenverfügbaren P festgestellt, was auf das Unvermögen der Lösungsmittel (CAT, CAL) zurückzuführen ist, FeP und AlP zu extrahieren. Daraus ergibt sich die Notwendigkeit, die Lösungsmittel zu modifizieren oder ein zusätzliches Lösungsmittel zu verwenden, um die Verfügbarkeit von Sekundär-P durch Kultursubstratanalysen zufriedenstellend zu charakterisieren. Um die Fähigkeit von P_{mod}, pflanzenverfügbares P zu charakterisieren, umfassender zu verstehen, wurde eine Bewertung unter Einbeziehung aller Versuchsdaten (einschließlich weiterer Probenahmezeitpunkte während der Kultur) sowie der nach der Ernte extrahierbaren P-Mengen (residual P_{mod}) vorgenommen. Es zeigte sich, dass unabhängig von den Zeitpunkten der Probenahme die Menge des pflanzenverfügbaren P im Kultursubstrat in gleicher Weise abbildbar war. Unter Ausschluss der Daten, für die eine Limitierung der Vorhersage von pflanzenverfügbarem P nachgewiesen werden konnte, ergab sich unter Berücksichtigung aller Versuchsdaten ein sehr enger Zusammenhang zwischen P_{mod} zu Versuchsbeginn und der P-Aufnahme der Pflanze + der zu Versuchsende extrahierbare P-Menge ($R^2 = 0{,}90$).

P_{mod} scheint ein vielversprechender Ansatz zur Charakterisierung der Pflanzenverfügbarkeit sekundärer P-Quellen für die Pflanzenproduktion unter Verwendung von Torfsubstraten zu sein und sollte zukünftig in Experimenten mit andere Pflanzen, weitere sekundären P-Quellen und Mehrkomponenten-Kultursubstraten validiert werden.

List of abbreviations

AlP	Aluminum phosphate
CAL	Extractant containing calcium-acetate-lactate
CAT	Extractant containing calcium chloride and diethylenetriaminepentaacetate
CaP	Calcium phosphate
CSH	Calcium silicate hydrate
COM	Green waste compost
DCP	Dicalcium phosphate
DG	Biogas digest
DGT	Diffusive gradients in thin-films technique
FeP	Iron phosphate
HAp	Hydroxyl apatite
ICP-OES	Inductively coupled plasma optical emission spectroscopy
M	Mass
MCP	Monocalcium phosphate
MgP	Magnesium phosphate
OCP	Octocalcium phosphate
P	Phosphorus
P_{AAC}	Alkaline ammonium citrate-soluble phosphorus
PbP	Lead phosphate
P_{CAL}	CAL-extractable amount of P in the growing medium
P_{CAT}	CAT-extractable amount of P in the growing medium
P_{FA}	2% formic-acid soluble phosphorus
P_{H2O}	Water-extractable phosphorus
P_{mod}	The amount of estimated plant-available P derived from a combination of P_{CAT} and P_{CAL}
P_{Olsen}	Extractable amounts of P by the Olsen-method
P_{total}	Aqua regia soluble phosphorus
RockP	Rock phosphate
rPUE	Relative phosphorus use efficiency
SS	Sewage sludge
SSA	Sewage sludge ash
SDG	Solid fraction of biogas digest
STR	Struvite
TCP	Tricalcium phosphate
TCR	Thermo-catalytic-reforming
V	Volume

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1. General introduction

1.1. Significance of phosphorus in plant production

Phosphorus (P) is an essential element for all living organisms. As structural element of biomolecules (e.g., DNA, phosphorylated fatty acids and sugars, and enzymes), it is involved in plant physiology (e.g., energy metabolism and cellular signaling) and plant growth (e.g., root architecture and organ development) (Figure 1). P deficiency in plants has a strong impact and results in a reduced growth, which is mainly caused by a disrupted energy metabolism (photorespiration, Calvin cycle) and its consequences (e.g., lack of mitosis). Besides a reduced growth, plants´ P deficiency symptom occurs as anthocyanosis, which is a result of upregulated biosynthesis of anthocyanins (Jiang et al., 2007).

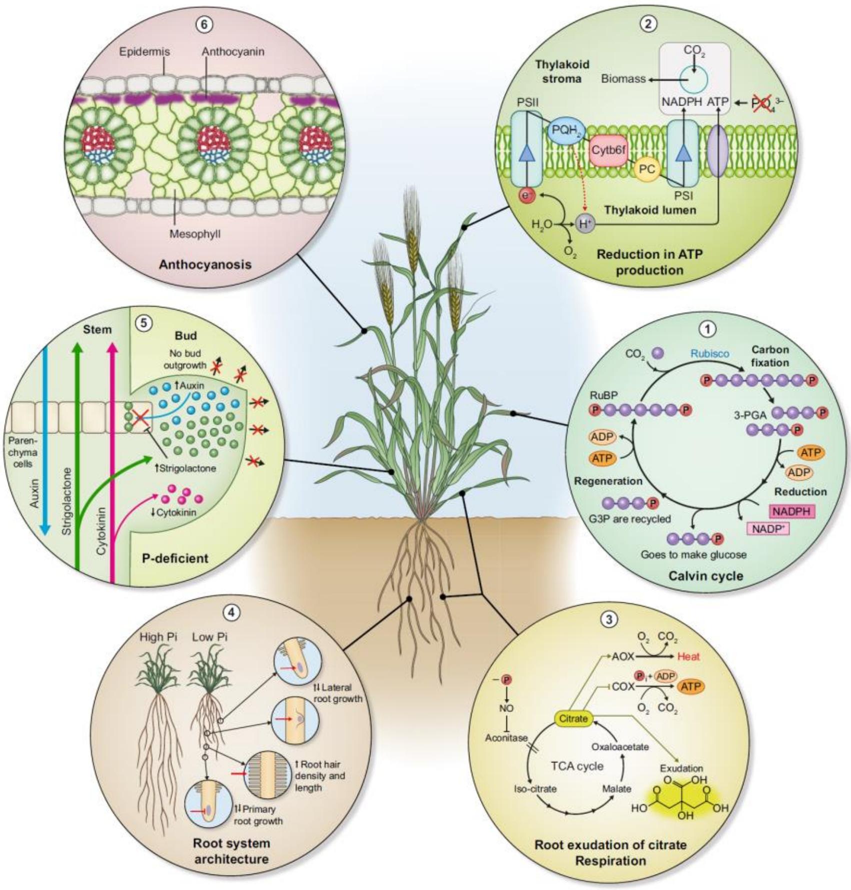

Figure 1: The role of P in plants according to De Bang et al., 2020.

In crop production systems, an adequate P supply to plants guarantees crop yield and quality (Wang et al., 2023). To avoid losses in yield and quality, plants must be empowered to absorb sufficient amounts of P through the soil solution. In natural soils the P concentration in the soil solution is not sufficient for optimal plant growth, since soil P reserves compounds in soil are mostly in a hardly soluble form (López-Bucio et al., 2000) for most soils. To overcome this limitation, the P pool of the soil used for crop production is anthropogenic increased by fertilization.

P fertilizers used in plant production systems are mainly produced from compounds of highly crystalline Ca-phosphates such as apatite which is the predominant mineral in mineable rock phosphate (RockP). About 80% of the mined RockP is used for fertilizer production (Scholz et al., 2019). During the past decades several depletion scenarios of the global RockP reserves and the geo-political accessibility have been controversly discussed. The global deposits of economically minable RockP will last approximately 300-400 years (Scholz et al., 2013) and include about 71,000 million tons (Statista, 2023). 70% of this commodity is located in Marocco (Statista, 2023), while other countries individually hold just 4.5%.

As Europe has no significant phosphate mines the European Commission addressed future RockP's scarcity by announcing it to be a critical raw material for European agri-economy, (Europeans list of critical materials, 2014). To address futures scarcity EU's action plan for a circular P economy was introduced to conserve finite RockP deposits and become less dependent from P imports. An important approach of this plan is to close the P cycle in agriculture by the reuse of P from waste streams as secondary source.

1.2. P rich waste streams and technologies for P recovery

There are many P-containing waste streams that, if properly exploited, have the potential to replace a significant portion of the P produced by traditional mining. Wiesler et al. (2020) reported that approximately 71% of the estimated amount of P needed for German plant production (533,000 t P year^{-1}) could be covered by farmyard and other organic residues. In this light, the most important secondary sources are liquid manure (202,000 t P year^{-1}), digests from biogas plants (73,000 t P year^{-1}), and as well as crop residues (74,000 t P year^{-1}), which are already on-farm used. According to these authors, other P rich waste streams, which are not properly reused until now, are: wastewater, by-products of animal production (slaughter wastes), and composts. Within these waste streams, wastewater offers the highest potential contribute closing P cycles. The authors reported that about 16,000 t P year^{-1} are already recovered from the German wastewater stream and reused in form of sewage sludge for agricultural purposes. However, the potential is likely to be much higher, since only a certain amount of P in the sewage sludge is used, while the rest is lost via aqueous discharges into water bodies. If probably exploited, the total potential of P recovery from wastewater is about 22% of the P required for plant production (Mihelcic et al., 2011). German slaughterhouse wastes as a byproduct of animal production contain about 17,000 t P year^{-1} (Wiesler et al., 2020), offering an unused pool for P recovery. However, according to Wiesler et al. (2020), 50% of this P pool is classified as hazardously matter, which poses a significant risk to the environment and human health. Therefore, the direct recycling of the P obtained in the animal by-products for plant production is to be seen as critical. Composts are another important secondary source for P, which has to be considered in plant production on arable land. On arable land, about 6,000 t year^{-1} P were directly applied for soil-based plant production (Wiesler et al., 2020). In addition to soil-based plant production, compost is also used in large quantities of approximately 1,600,000 m^3 year^{-1} (IVG, 2023) as a growing medium constituent in soilless production. Under consideration of an average dry bulk density of 400 g L^{-1} (Amberger-Ochsenbauer and Meinken, 2022) and a total P content of 0.22% (Kehres and Grantzau, 2022), this corresponds to approximately 1400 t P. The direct use of these secondary P sources as fertilizer is often limited by negative properties of the raw materials, such as a low economic transportability, abundance of contaminants such as heavy metals and organic pollutants, or pathogens (Harrison et al., 2006; Baize, 2009; Magri et al., 2019). Nevertheless, these sources have a high potential for P recycling (Ye et al., 2017), and several technologies for P recovery from liquid and solid wastes have been developed over the last decade (Kabbe et al., 2015).

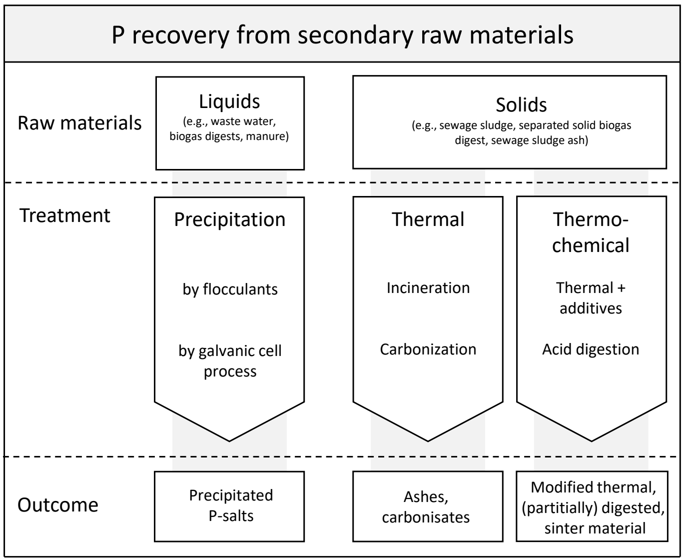

Figure 2. Overview of important pathways of P recovering from secondary raw materials.

In liquid waste streams (e.g., manure, and biogas digest), P is present to large shares as dissolved phosphate in the aqueous phase, which can be easily recovered by precipitation using flocculants (e.g., Al-, Fe-, Ca- or Mg-compounds) or a galvanic cell. The outcome of such precipitation processes can be aluminum phosphate (AlP), iron phosphate (FeP), calcium phosphates (CaPs) of different crystallinity or magnesia phosphates (MgPs) for which struvite (magnesia ammonium phosphates) is the most common. However, recovering P from the aqueous phase via precipitation covers only a certain proportion of the total amount of P contained in liquid waste stream. Besides P being present in the aqueous phase, the remaining is located in the solid phase. To enhance the recovery rate of P from liquid waste streams, the P contained in the solid phase can be (i) leached by acid digestion and subsequently precipitated, or (ii) solids can be separated to apply P recovery technologies suitable for solids. By applying thermal energy (incineration and carbonization) to solid organic wastes, volatile elements (e.g., N, C, and Hg) are gaseous removed while P and other non-/semi-volatile elements (e.g., K, Mg, Cd, and Pb) are subsequently concentrated as highly stable compounds contained in the resulting product (ashes or carbonisates). To further improve product quality by heavy metal elimination, thermal process modifications are required. Halogenic compounds (e.g., $MgCl_2$, $CaCl_2$), used as additive during the thermal treatment, decreases the total heavy metal content by the formation of volatile metal-halides. However, additives are also used to shift the P-bearing phase from highly stable, crystalline but less plant-available P species to compounds of higher availability. For example the application of Na-compounds (e.g., Na_2SO_4, Na_2CO_3) as additive in thermal processing lead to P-bearing phase containing high proportions of NaCaP-forms which are known for a better plant availability (Steckenmesser et al., 2017). Another method to achieve an increased plant-available P–bearing phase is – analogously to conventional RockP-based fertilizer production – the acidulation of the material. By using acids, crystalline and hardly plant-available P compounds such as apatites (CaP) are protonated and thus transformed into structures of less crystallinity and higher bioavailability.

Overall, technologies for P recovery from secondary sources result in a wide range of products with different chemical structure. To establish such products as fertilizer in plant production, products need to be environmentally safe, the value chain must be economically feasible, and P availability to plants needs to meet the requirements of crop production systems.

1.3. Evaluation of plant availability of secondary P sources for crop production systems

Biotests with sensitive model plants are - without any doubt - indispensable to evaluate the plant availability of a fertilizer, since they make the P fertilization effects on plant growth and development measurable. However, as outlined by Kratz et al. (2019), the outcome of such biotests strongly depends on the P source and trial type, respectively. Thus, a comparative interpretation of results obtained from different trials is indeed quite prone to misleading conclusions. In this light, these authors reported the following characteristics of plant trials as essential to be considered for evaluation of plant P availability for plant production based on arable land: (I) characteristics of soil since P dynamics in soils and thus plant-available P in the soil solution is strongly influenced by e.g., soil pH, and P buffer capacity; (II) duration of the trials, since P demand for plants varies among plant development stages and the dissolution processes of applied P-forms differs over time; (III) plant species, since species exhibit different abilities to access soil-P; (IV) particle size of applied fertilizers, since smaller particle sizes provide greater reaction surfaces for solution processes impacting P dynamics.

Over the past decades, the plant availability of P from secondary sources has been studied for mineral soil-based crop production via different pot and field trials (Römer, 2006; Appel and Friedrich, 2017; Lemming et al., 2017; Vogel et al., 2017; Wollmann et al., 2018). As summarized by Kratz et al. (2019), plant availability of secondary P sources exhibits wide variability, since the contained P-species differ widely and are often coincidently present in different proportions.

Beside soil-based plant production, other cropping systems of economically relevance use soilless growing media. In 2022, 8.1 million cubic meters of growing media were produced in Germany (IVG, 2023), primarily composed of peat, but also of organic and mineral peat substitutes (e.g., wood fiber, compost, and clay). The usage of P obtained from secondary sources for growing media’s base fertilization could help preserve the global finite RockP resources. However, the conditions of growing plants differ significantly between growing media- and soil-based production and thus may the requirements of fertilizers’ availability. In contrast to mineral soil-based cropping systems, crops cultivated in production systems using peat-based growing media usually exhibit a short cultivation time (e.g., few weeks for bedding plants) and plant species cultivated in soilless production differ significantly from those of arable land. In addition, peat as growing medium nearly lacks the ability to buffer P, which results in different P dynamics compared to soils (Khandan-Mirkohi and Schenk, 2009). Thus, transferability of knowledge about plant availability of secondary P sources from soil to soilless production is questionable. The lack of investigations covering evaluation of plant P availability of secondary sources under the specific conditions of growing media-based plant production evidenced the urgent need of research in this field. However, despite plant trials` ability to characterize the plant availability of secondary P sources, they are too time consuming and costly for routine analyses. Cheaper and time efficient methods for a suitable prediction of plant P availability may help to introduce new fertilizer products in cropping systems.

1.4. Prediction of plant-available P from secondary sources

Static extraction with different solvents (e.g., formic, or citric acid) is used in routine fertilizer analytics to obtain insights about the fertilizer's solubility, which corresponds to its plant availability. Historically, those static extractions were individually developed and validated for a specific type of fertilizer which predominantly consists of a single P compound. In contrast, fertilizers based on secondary P sources show a great heterogeneity of contained P species which are in addition abundant in different proportions (Kratz et al., 2019). Thus, classical assessment of plant-available P by fertilizer analysis faces the problem of capturing the availability of this heterogeneity in P-species and mixing ratios (Duboc et al., 2022). In addition, static fertilizers extractions display another vulnerability in predicting plant-available P. Hence, fertilizer extraction displays a fixed amount of soluble fertilizer-P, determined by the parameters of the extraction method itself (e.g., extraction solvent, extraction ratio, etc.), it cannot reflect the dynamic P solubility of secondary sources in different soils with e.g., various levels of pH or buffer capacity. Therefore, methods including fertilized soil (standard soil P tests) seem to be more promising to predict plant P availability under field conditions. For soil-based production systems several standard soil tests (e.g., calcium-acetate-lactate (CAL)-method, sodium bicarbonate (Olsen)-method) have been evaluated to predict the pool of plant available P in soil fertilized with secondary sources (Zeggel et al., 2015; Duboc et al., 2017; Kratz et al., 2019). According to Duboc et al. (2017) and Zeggel et al. (2015), the extractable amount of P using the CAL-method (P_{CAL}) was correlated to the P taken up by plants, ranging from 0.57 to 0.88 for the coefficient of determination. However, it must be noticed that the relationship differs among soil pH and type of secondary P source. For secondary P sources containing high proportions of highly crystalline CaPs (e.g., like composts or Ca precipitates), the P_{CAL} overestimates plant availability of such P species in neutral or alkaline soils (Zeggel et al., 2015). Hence, the solvent CAL is strongly buffered at pH 4.1, CaPs of higher crystallinity - hardly soluble under neutral or alkaline soil conditions - are dissolved and extracted.

Opposite to CAL, the extraction solution with bicarbonate is strongly alkaline buffered at the pH of 8.5. Strong relations ($R^2 = 0.88$) between plant P uptake and extractable P amounts in the soil using the Olsen-method (P_{Olsen}) was shown by Duboc et al. (2017) for a variety of different secondary P sources in a growth trial using a slightly acidic soil. However, it seems improbable that P_{Olsen} can reflect plant availability of secondary P sources containing high amounts of CaPs of higher crystallinity for strongly acidic soils, due to its inability to extract relevant amounts of CaPs at pH 8.5.

The results obtained from work with soil P tests indicate that a large part of the available P pool obtained from fertilizing secondary sources, can be reflected under conditions of soil-based plant production. However, a single, static extraction method is not suitable to satisfactorily predict secondary sources plant availability, and thus implies the need for dynamic approaches (Kratz et al., 2019; Duboc et al., 2022). In this light, the soil-P method based on diffusive gradients in thin films (DGT) technology reflects such an dynamic approach. In contrast to CAL or Olsen-method, the DGT is extracting at the actual soil pH, using an adsorbing resin disk, which shall mimic the plant uptake of P from soil solution. Duboc et al. (2017) found excellent correlations ($R^2 > 0.9$) between extractable amounts of P by the DGT-method and the dry matter and P content of plants in using several secondary P sources. These observations are further supported by the findings of Vogel et al. (2017), which indicate DGT as a promising method to predict P availability of secondary sources for soil-based cultivation. However, sample preparation is complicated and time consuming, since the fertilized soil needs to be incubated for several weeks to obtain suitable DGT values. Therefore, DGT as time efficient routine soil test seems to be not feasible.

Unlike for mineral soil-based crop production, for soilless crop production using peat as a growing medium there is a lack of studies to predict P availability from secondary source fertilizers. Since P dynamics in peat differ significantly from those in soils, the transferability of findings from soil-based to soilless cultivation is questionable. In Germany, the prediction of plant available P in growing media is based on two commonly applied extractions using CAL or calcium chloride + diethylenetriaminepentaacetate (CAT) as solvent. The CAT method reflects readily soluble P, but underestimates the less soluble reserves (Alt et al., 1994). In contrast, the plant availability of CAL-extractable P is often overestimated, particularly when sparingly soluble calcium phosphates of higher crystallinity, which are the predominant P compounds in RockP or composts (Frossard et al., 2002; García-Albacete et al., 2012), are fertilized or when the growing media are rich in clay and have high pH (Alt et al., 1994; Handreck, 1996). A reliable assessment of the plant-available P pool in growing media fertilized with secondary sources is an important key to introduce such innovative fertilizers in horticultural production and is an urgent need for a sustainable fertilization management related to the plant’s nutrient demand.

2. Thesis object and outline

This thesis investigates the plant availability of secondary P sources for horticultural crop production based on peat-based growing media and the possibility to characterize plant-available P from secondary sources by standard growing media analyses.

The structure of this thesis is cumulative, containing three sections.

Section I covers the plant availability of different secondary P sources (untreated residues, thermal or thermochemically treated residues, and precipitation products) for plant production using peat-based growing media. In addition, standard growing media analyses are discussed in respect of their feasibility to estimate available secondary sources-P. This section contains one published article.

Section II covers the plant availability of secondary P sources (digest, ashes, biochars, cinder product and struvite) in growing media under contrasting pHs. This section contains two published articles and data from an unpublished pot trial.

The effects of contrasting pH in growing media on plant availability were shown in a trial conducted in winter season for different exemplary selected secondary P sources (untreated biogas residuals, sewage sludge ash, cinder product and a struvite) under conditions more closely related to horticultural practice (growing media preparation and pot filling by volume) and in a trial, conducted with two additional biochars under more controlled conditions (growing media preparation and pot filling by weight). In addition, several sewage sludge ashes of different origin were tested regarding their plant availability under contrasting pH conditions.

For the data of the unpublished trial and the sewage sludge ash trial, the prediction model based on P_{CAL} and P_{CAT} is discussed in respect of its feasibility to satisfactorily characterize available secondary source-P.

Section III covers the effect of grain size of selected secondary P sources (biochar, ash, cinder product, and struvite) and the suitability of the P_{CAT}- and P_{CAL}-based prediction model to characterize P availability in soilless production. This section contains one published article and data of an unpublished plant trial.

3. Material and methods

The following paragraphs include summarized information about the materials and methodologies, and the experimental set ups used in the sections I-III.

3.1. Secondary P sources and reference fertilizers

In this thesis, 22 secondary P sources were investigated, which are divided by their processing procedure into 4 subgroups: untreated organic feedstocks (untreated), thermally processed feedstocks (thermal treated) and thermochemically treated feedstocks (thermochemically treated), and precipitates from liquid waste streams. The following contains a brief grouped (untreated, thermal, thermochemical, precipitates) description of the test fertilizers. A visual impression of the applied secondary P sources is given at the end of the 3.1.

Untreated feedstocks

5 untreated organic feedstocks were investigated (three biogas digests, one sewage sludge, and one compost). The biogas digests 1 and 2 (DG1, DG2) derived from mesophilic digestion of manure and clover grass, differ as DG2 digested corn crop mix, unlike DG1 with a whole grain mixture. The liquid digests were dried at 105°C and subsequently milled (swing mill) to obtain a powdery material suitable for homogeneous application into the growing medium. In addition, a pelletized, separated solid fraction of a biogas digest (SDG) obtained from slurry, corn-/grain silage was investigated. The pellets of SDG were milled analogously to DG1 and DG2 to obtain an admixable fine structure. To investigate sewage sludge, a dried sewage sludge (SS) was obtained from the wastewater treatment plant Klaerwerk II (Nuremberg city). The sewage sludge of Klaerwerk II arises after municipal wastewater processing, which includes P elimination using Fe-salts and a subsequently stabilization of the organic sludge phase by microbiological digestion. The last untreated organic feedstock included in the investigations was a commercially available green waste compost (COM), which was obtained from a growing media producer (Patzer Erden GmbH, Sinntal-

Altengronau, Germany). The applied form of the untreated organic feedstocks is displayed in Figure 3.

Thermally treated feedstocks

In sum nine secondary P sources obtained from thermal treatment without further treatment (3 biochars and 6 sewage sludge ashes) were investigated. Two biochars (BC-SDG400 and BC-SDG700) were obtained by Pyrolysis of SDG in a TCR (thermo-catalytic-reforming)-pilot plant. The TCR-process is a two-stage pyrolysis process (adjustable process temperatures) that converts biomass into biochar, hydrocarbon fractions (gaseous, liquid), and water. For SDG-based biochars, the first step of pyrolysis was at 700°C, and the second step at 400°C for SDG-BC400 and at 700°C for SDG-BC700. In contrast to these SDG-biochars, the last biochar (BC-650) was produced by the one-step pyrolysis (650°C) in a pilot Pyreg reactor using sewage sludge as input material. In addition to the pyrolyzed sewage sludge, the studies include mono-incinerated sewage sludges (850-950°C), which were obtained by different German suppliers: (i) wastewater treatment plant Trollins/Steinhaeule by Neu-Ulm city; (ii) Ostrauer Kalkwerke GmbH, Ostrau city; Innovatherm GmbH by Luenen city, (iii) and wastewater treatment plant Gut Grosslappen by Munich city. Sewage sludge used for incineration was for the majority of the SSAs ($\mathrm{SSA_{Trollins}}$ batches 1-3, $\mathrm{SSA_{Ostrau}}$, $\mathrm{SSA_{Grosslappen}}$) derived from treatment of municipal wastewater without or with negligible amounts of industrial wastewater. In contrast, $\mathrm{SSA_{Luenen}}$ originated from sludge of municipal and industrial wastewater treatment.

For all origins - except Ostrau – sewage sludge ash production was done by incineration in a fluidized bed oven with subsequently milling of the ashes to fine powder. In contrast, $\mathrm{SSA_{Ostrau}}$ was produced using as rust furnace with no additional post-treatment, which resulted in a coarser product. $\mathrm{SSA_{Ostrau}}$ was milled analogously to the DGs to obtain a structure comparable to the other SSAs.

Thermochemically treated feedstocks

Three sewage sludge-based secondary P sources of different thermochemically treatments were included in the investigations, namely ASHDEC, MEPHREC-SS, and SERAPLANT. ASHDEC represents a glown phosphate of powdery structure produced according to the AshDec-process using a rotary furnace co-incinerating SSA and Na_2SO_4 at 950°C. The fertilizer was produced and supplied by Outotec GmbH und Co KG (Oberursel, Germany). MEPHREC-SS as coarse-grind vitreous secondary P source represents another product of thermal treatment using solid additives. However, in comparison to ASHDEC, MEPHREC-SS is produced at higher temperatures (1600°C) in a metallurgic process using coke, SS, and lime as input materials. MEPHREC-SS was obtained from a pilot blast furnace of the company Klaerschlammverwertung Region Nuremberg GmbH onside the wastewater treatment plant Klaerwerk 2 in Nuremberg city. In contrast to secondary P sources based on thermal treatment including additives during the thermal process (MEPHREC-SS, ASHDEC), the fertilizer SERAPLANT is produced by partial acidulation of mono incinerated sewage sludge. Using H_3PO_4 within a spray granulation process, the SSA is firstly P enriched and secondly partially acid digested while simultaneously being formed to fertilizer granules. To ensure SERAPLANT can be uniformly admixed into growing media, the granules were milled to a powdery structure analogously to the biogas digests. SERAPLANT was provided by the SERAPLANT GmbH (Haldensleben, Germany).

In contrast to the rest of this thesis, in the published pretrials (pH trail 1, grain size trial 1), the abbreviation Mephrec was used for MEPHREC-SS.

Precipitates from liquid feedstocks

In total 5 secondary P sources obtained from different P-precipitation approaches were part of the investigations namely PROC, STR-AIRPREX, STR-STUTTGART, STR-GALV, STR-SLURRY. Most of the precipitates (PROC, STR-AIRPREX, STR-STUTTGART, STR-GALV) were obtained by P recovery from wastewater. PROC, a crystallization product with a granular structure (diameter <1 mm) was developed and supplied by the Karlsruhe Institute of Technology (Karlsruhe, Germany). The P-RoC process uses calcium silicate hydrate (CSH) as seed material and pH raising agent in a reaction tank containing wastewater to crystallize P-salts (apatitand struvite-forms) on the CSH-material surfaces. STR-AIRPREX is a commercially available fertilizer consisting of struvite crystals of few mm sizes, which was produced and supplied by the Berliner Wasserbetriebe (Berlin, Germany). STR-AIRPREX was obtained from the AirPrex-process using for struvite formation $MgCl_2$ as flocking agent and a CO_2-stripping of the liquid phase of digested sewage sludge for pH adjustment (pH 8–10). In contrast to STR-AIRPREX, STR-STUTTGART was obtained by a more complex procedure (Stuttgart-process). For struvite precipitation MgO is used as flocculant and pH rising agent in liquid sewage sludge, which was antecedently digested with H_2SO_4 and treated with the chelator citric acid for heavy metal reduction. STR-STUTTGART of powdery structure was produced and supplied by MSE Mobile Schlammentwaesserungs- und Entsorgungsgesellschaft mbH (Zwickau, Germany). A struvite precipitation technique without a classical flocculant was used to produce STR-GALV. This powdery struvite-product was precipitated in a galvanic cell using an Mg-sacrifice anode. STR-GALV was developed and supplied by Fraunhofer Institute for Interfacial Engineering and Biotechnology (Stuttgart, Germany). In contrast to the other investigated precipitates, STR-SLURRY was derived from pig manure by addition of NaOH/KOH as pH raisin agent to precipitate struvite and calcium phosphates. STR-SLURRY was supplied by Fraunhofer Institute for Interfacial Engineering and Biotechnology (Stuttgart, Germany).

Visual impression of the applied secondary P sources and the chemical characterization

The visual appearance of the secondary P sources ranged from powdery organic material to minerals in crystal in shape of few mm. Among the investigation different fractions of specific secondary P sources were investigated in plant trials. Figure 3 displays a visual expression of structure for all forms of tested secondary P sources applied in the studies. In addition, for SSAs detailed information about the particle size distribution are available in section II, SSA comparison trial.

In Table 1 the chemical characterization of secondary P sources is given.

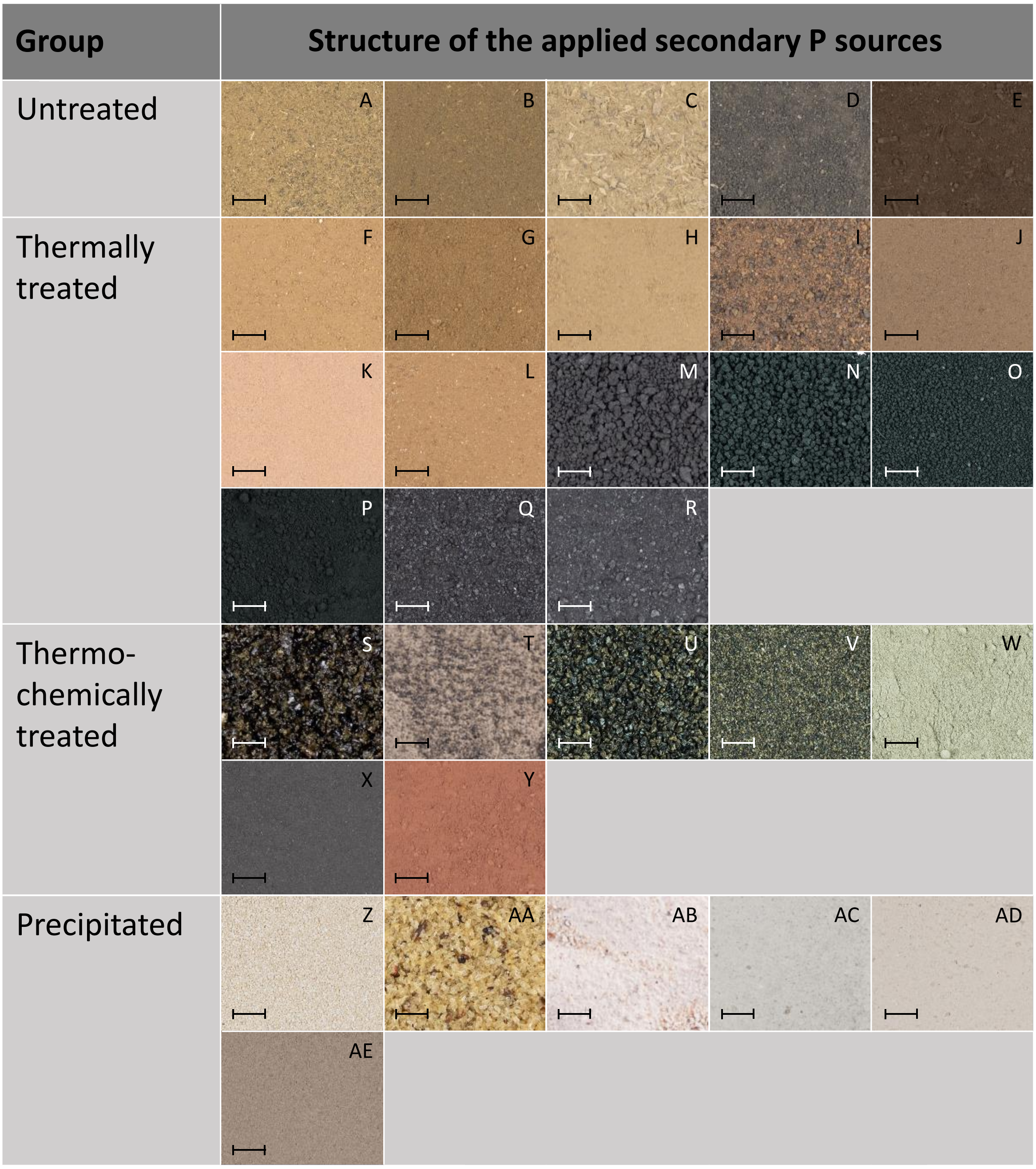

Figure 3: Groupwise visual impression of the secondary P sources. Untreated: A = DG1, B = DG2, C = SDG, D = SS, E = COM; thermal treated: F = SSA$_{\text{Trollins1}}$, G = SSA$_{\text{Trollins2}}$, H = SSA$_{\text{Trollins3}}$, I = SSA$_{\text{Ostrau}}$ as received, J = SSA$_{\text{Ostrau}}$ milled, K = SSA$_{\text{Luenen}}$, L = SSA$_{\text{Grosslappen}}$, M = BC-650 as received, N = BC-650 milled to 1-2 mm, O = BC-650 milled to 0.3-0.5 mm, P = BC-650 <0.2 mm, Q = BC-SDG400, R = BC-SDG700; thermochemically treated: S = MEPHREC-SS as received, T = MEPHREC-SS milled, U = MEPHREC-SS milled to 1-2 mm, V = MEPHREC-SS milled to 0.3-0.5 mm, W = MEPHREC-SS milled to <0.2 mm, X = ASHDEC, Y = SERAPLANT; precipitated: Z = PROC, AA = STR-AIRPREX as received, AB = STR-AIRPREX milled, AC = STR-STUTTGART, AD = STR-GALV, AE = STR-SLURRY; scale bar = 5 mm.

Table 1: Description of the secondary phosphorus sources tested, sorted by the type of feedstock treatment, and their chemical characterization according to the German fertilizer ordinance. Aqua regia-soluble phosphorus (P) (P_{total}) is expressed in milligrams per gram of dry matter, and water-soluble P (P_{H2O}), alkaline ammonium citrate-soluble P (P_{AAC}), and 2% formic acid-soluble P (P_{FA}) is expressed as the percentage of P_{total}. Based on structural elucidation analysis, P-bearing phase of the tested secondary sources P species is indicated as outlined in literature.

Description of the tested secondary P sources			**Chemical characterization**					
Group	**ID**	**Process reference**	**P_{total}**	**P_{H20}**	**P_{AAC}**	**P_{FA}**	**Suspected P-species**	**Reference**
			mg g^{-1}	Percentage of P_{total}				
Untreated	DG1	-	8.7	23	91	91	Heterogenous P-phase in digestates: DCP, struvite, FeP, HAp	Güngör and Karthikeyan (2008), Bruun et al. (2017)
	DG2	-	16.1	34	80	97		
	SDG	-	11.1	51	100	94		
	SS	-	30.9	1	78	77	Heterogenous P-phase in SS (mainly driven by P-elimination during wastewater treatment): CaP of different crystallinity (DCP, TCP, OCP, Ap), FePs (vivianite, lipscombite), polyphosphates and phosphorlipids	Frossard et al. (1997), Huang and Shenker (2004), Huang and Tang (2015), Steckenmesser et al. (2017)
	COM	-	3.1	10	100	94	CaP of higher crystallinity (OCP, Ap) and organic P	Frossard et al. (2002)
Thermal treated	$SSA_{Trollins1}$	-	67.0	0	28	67	Heterogenous P-phase in SSAs (mainly driven by P-elimination during wastewater treatment): CaP of higher crystallinity (TCP, whitelockite, HAp), Fe- and AlP and other (heavy) metal associated P	Ohbuchi et al. (2008), Peplinski et al. (2015), Nanzer (2012), Steckenmesser et al. (2017), Vogel et al. (2020)
	$SSA_{Trollins2}$	-	58.5	0	28	84		
	$SSA_{Trollins3}$	-	59.9	0	28	68		
	SSA_{Ostrau}	-	88.6	0	20	52		
	SSA_{Luenen}	-	22.4	0	15	76		
	$SSA_{Grosslappen}$	-	96.4	0	23	61		
	BC-650	Appel and Friedrich (2017)	4.6	0	17	11	TCP (whitlockite)	Appel and Friedrich (2017)
	BC-SDG400	Stenzel et al. (2015)	22.8	5	83	86	heterogenous P-phase in digestate-chars: CaP of different crystallinity (DCP, TCP, HAp), struvite, FeP, pyrophosphate	Bekiaris et al. (2016), Bruun et al. (2017)
	BC-SDG700	Stenzel et al. (2015)	31.5	3	46	76		
Thermochemically treated	ASHDEC	Huvukainen et al. (2016)	75.1	1	77	89	Ca-alkali-phosphates	Stehmann et al. (2015)
	MEPHREC-SS	Hagspiel (2019)	19.1	0	2	47	-	-
	SERAPLANT	Weigand et al. (2013)	158.8	51	97	78	CaPs (MCP, DCP), Fe-/AlP, MgP (newberyite)	Vogel and Adam (2011)
Precipitated	PROC	Berg et al. (2005)	40.4	2	86	100	Mainly CaP of high crystallinity (HAp), struvite	Ehbrecht et al. (2009), Ehbrecht et al. (2016)
	STR-AIRPREX	Kabbe et al. (2015)	103.8	3	14	100	Mainly struvite, small amounts of other P-forms (e.g., CaP)	Marti et al. (2010)
	STR-STUTTGART	Krämer and DPP e.V. (2019)	102.4	6	13	100		
	STR-GALV	Bilbao (2014)	97.3	0	4	101		
	STR-SLURRY	Bilbao (2017) pers. commun.	111.9	2	26	100	Struvite, CaP	Daumer et al. (2013), Bilbao (2017) pers. commun.

CaP = calcium phosphate, MCP = monocalcium phosphate, DCP = dicalcium phosphate, TCP = tricalcium phosphate, OCP = octocalcium phosphate, Ap = apatite, HAp = hydroxy apatite, FeP = iron phosphate, AlP = aluminum phosphate, MgP = magnesium phosphate, SS = sewage sludge, SSA = sewage sludge ash

Reference fertilizers

As fully plant available P-form, a water-soluble MCP ($Ca(H_2PO_4)_2 \cdot H_2O$, analytical grade, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany) was used. To ensure a uniform distribution of MCP-P in the growing medium, MCP was applied as solution and evenly admixed into the growing medium. In contrast to the highly processed MCP, fertilizer granules of a finely ground (90% <100 µm) RockP (Hyperphos, producer unknown) was used as a hardly plant-available P-form. RockP granules were ground in a swing mill as already mentioned for the secondary P sources to obtain a powdery structure, suitable for homogenously admixing into the growing medium.

In contrast to the rest of this thesis, in the published pretrials (pH trail 1, grain size trial 1), the abbreviations rock-P or Hyperphos were used for RockP and for MCP, the abbreviation CaP was used.

3.2. Plant trials

For the plant trials Baltic white peat low in available nutrients (PATZER ERDEN GmbH, Sinntal-Altengronau, Germany) were used for growing medium blends. To adjust the pH level of the growing medium according to the specific experimental conditions (Table 2), lime (85% $CaCO_3$; Zement- und Kalkwerke Otterbein, Grossenlueder-Mues, Germany) was mixed into the white peat. Growing mediums P free base fertilization (in mg L^{-1}) was provided using a custom P-free fertilizer blend (19-0-19 including trace elements) based on 200 mg N L^{-1}. The ratio of NH_4-N:NO_3-N was approximately 1:3. For P fertilization of the growing medium a homogenized portion of the water-insoluble P sources (secondary P sources or RockP) or dissolved MCP were evenly admixed into growing medium portions. The aimed targeted P supply was for all experiment approximately 70 mg P L^{-1} (equivalent to 25 mg P pot^{-1}). Fertilized growing media were usually filled into pots by weight to ensure the same amount of P was given to all plants. In contrast, in the pretrials (pH trial 1, grain size trial 1), the growing media were filled into pots by volume according to good horticultural practice, as a trade-off between resource management (materials, time, etc.) and the scientific accuracy. However, a precise and equal P supply between different pots may not be guaranteed by this procedure.

After pot filling, precultivated plants were transplanted into the pots.

As model plant marigold was used since it represents an ornamental typically for growing media-based plant production and for its strong sensitivity for P deficiency (Khandan-Mirkohi and Schenk, 2009; Ehmann et al., 2019). As cultivar *Tagetes patula* x *erecta* 'Zenith Red' (Floranova Ltd., Foxley, UK) was selected, showing the strongest symptoms for P deficiency (anthocyanosis and reduction in plant growth) in plant trial (data not shown) comparing different cultivars. For the experiments marigolds seeds were sown in a weakly fertilized peat (70 mg N, 40 mg P, and 75 mg K L^{-1}) limed to pH of 5.5. After 10 to 14 days single seedlings reached a prickable state and were transplanted into plastic pots (diameter 10 cm, volume 400 mL; Teku, Poeppelmann Kunststoff-Technik GmbH & Co. KG, Lohne, Germany) individually. Among the greenhouse trials, pots were arranged into four replicates. The number of plots per treatment differed within the range of 32 to 52 pots throughout the experiments (Table 2) due to space limitation in the greenhouses.

During cultivation, plants were irrigated with deionized water according to good horticultural practice. Throughout the experiments plants were fertilized (P free multi nutrient fertilizer: 19-0-19 including trace elements) according to the estimated weekly plant demand derived from pervious trials (data not shown). As required, a fertilizer solution was supplied at doses of 20 mg N per pot. To avoid losses of nutrients through leaching, saucers were placed under pots and occurring draining water were poured back into the pots. In addition, saucers were flushed twice during the duration of the experiments.

The duration of the trial was based on the plants reaching the marketable stage for ornamental cultivation. Plants were considered marketable when the first flower had just opened or when some flowers had opened but no flower had faded. Time period for reaching these flowering states ranged between four to seven weeks between the trials (Table 2) depending on experiments were conducted on summer and winter. For trials conducted during winter plants were additional lighted for 12 hours at a base of 50 µmol m^{-2} s^{-1} (Philips SON-T Agro 400W, Phillips, Hamburg, Germany).

Greenhouses’ temperature heating was adjusted to temperatures ranging between 18–22°C for heating and 23–25°C for ventilation. For pest control (minier flies, soft-bodied mites, or thrips) plant protection agents (Table 2) were applied according to good horticultural practice.

Table 2: Overview of the conducted experiments

Thesis structure	Trial	Time	Treatment information	Pots per treatment	Greenhouse temperature settings	Plant protection
Section I (Screening)	Screening (published)	4 weeks during summer	Control: MCP Fertilizer: DG1, DG2, COM, SDG, SS, $SSA_{Trollins1}$, BC-650, BC-SDG400, BC-SDG700, ASHDEC, MEPHREC-SS, SERAPLANT, PROC, STR-AIRPREX, STR-STUTTGART, STR-GALV, STR-SLURRY	48	Heating: 22/20°C (day/night) Ventilation: 25°C	3 x 0.1% Vertimec (Syngenta, Basel, Switzerland)
Section II (pH level)	pH trial 1 (published)	6 weeks during winter	Control: MCP, RockP Factors: pH x fertilizer Fertilizer: $SSA_{Trollins1}$, MEPHREC-SS, STR-AIRPREX pH: 4.5, 6.0	48	Heating: 20/18°C (day/night) Ventilation: 23°C	3 x 0.1% Vertimec (Syngenta, Basel, Switzerland)
	pH trial 2 (unpublished)	4 weeks during summer	controls: MCP, RockP Factors: pH x fertilizer Fertilizer: DG1, $SSA_{Trollins1}$, BC-650, BC-SDG400, MEPHREC-SS, STR-AIRPREX pH: 4.5, 6.0	32	Heating: 22/20°C (day/night) Ventilation: 25°C	3 x 0.1% Vertimec (Syngenta, Basel, Switzerland)
	SSA comparison trial (published)	4 weeks during summer	controls: MCP, RockP Factors: pH x fertilizer Fertilizer: $SSA_{Trollins1}$, $SSA_{Trollins2}$, $SSA_{Trollins3}$, SSA_{Ostrau}, SSA_{Luenen}, $SSA_{Grosslappen}$ pH: 4.5, 6.0	48	Heating: 22/20°C (day/night) Ventilation: 25°C	3 x 0.075% Conserve (Corteva Agriscience Germany GmbH, Munich, Germany)
Section III (Grain size)	Grain size trial 1 (published)	7 weeks during winter	Control: MCP Factors: Grain size x fertilizer Fertilizer: STR-AIRPREX, SSA_{Ostrau}, MEPHREC-SS, RockP Grain size: Coarse (as received), fine (milled to powder)	52	Heating: 20/18°C (day/night) Ventilation: 23°C	3 x 0.1% Vertimec (Syngenta, Basel, Switzerland)
	Grain size trial 2 (unpublished)	4 weeks during summer	Control: MCP Factors: Grain size x fertilizer Fertilizer: BC-650, MEPHREC-SS Grain size: <0.2 mm, 0.3-0.5 mm, 1-2 mm	48	Heating: 22/20°C (day/night) Ventilation: 25°C	3 x 0.1% Vertimec (Syngenta, Basel, Switzerland)

3.3. Data collection

At harvests, vegetated pots of a treatment were pooled per replicate. The above-ground shoot fresh weight was determined, and after subsequently drying at 70°C in a forced-air oven dry weight was recorded after biomass reached weight constancy. For analyses of P content, dried plant material was ground to particle sizes <0.5 mm using a centrifugal mill (ZM1, Retsch, Haan, Germany) and digested in an HNO_3/H_2O_2-solution under pressure in a microwave oven (Multiwave ECO, Anton Paar, Graz, Austria) according to Miller (1998). Subsequently, P in the digestion solution was determined using ICP-OES (wavelength: P 213.6 nm; iCap 6000 DV, Thermo Fisher Scientific, Dreieich, Germany). In addition, P uptake of plants was calculated by multiplying plants P content with dry weight. The plant P uptake as percentage of applied P was defined as the relative P use efficiency (rPUE).

Growing media analyses for soluble P were performed at trail starts and harvest times. Two extraction methods were used to characterize soluble P in growing media, namely CAL-method and the CAT-method. The amount of CAL-soluble (P_{CAL}) in the growing medium was analyzed according to VDLUFA-method A 6.2.1.1 (Kießling and Hofmann, 2016), and the CAT-soluble phosphate (P_{CAT}) in the growing medium according to VDLUFA-method A 13.1.1 (Alt and Hofmann, 2004), respectively. Determination of P in growing media extracts was done via ICP-OES analogously to plant analyses.

For quality assurance of analytical data, sample duplicates were performed, and reference material was used. If unexplainable differences between results derived from sample duplicates occurred, analyses were repeated. Operation of the analytical instruments was done according to the manufacturers' user manuals.

3.4. Statistical analysis and modelling of plant P uptake

Statistical analysis of the data derived from plant trials were performed using Minitab V18 (Minitab Inc., State College, PA, USA). Data visualization was done with MS Excel 2016 (Microsoft Corporation, Redmond, WA, USA) and *ggplot2* package (Wickham, 2016) for R programming language v. 4.0.2 (R Development Core team, 2008).

For statistical evaluation of parameters derived from plant growth and analysis, respectively, an analysis of variance (ANOVA) was performed to identify differences between the treatments. In cases of a two factorial trial design two-way ANOVA was performed. If an interaction was found between different factors, the data sets were divided by factor level and an one-way ANOVA was calculated for each level. If ANOVA exhibited significant differences, Dunnett's test was used to identify differences of secondary P treatments against a control fertilizer, or Tukey's test was used to identify differences within specific treatments. Level of statistical significance used in tests was $p < 0.05$ unless otherwise stated.

To evaluate the relation between plant P uptake and extractable amount of P in the growing medium (P_{CAL}, P_{CAT}, respectively) scatter plots and regression analysis as well as t-test were used. An innovative approach to characterize the plant-available P pool in the growing medium was carried out by combining the CAL- and CAT-extractable P amounts. The combination was performed under the assumption that: a) the CAT-extractable amount of P reflects the readily amount of plant-available P, but will underestimate hardly soluble P pools that are plant available over time; b) the hardly soluble, but plant-available P is CAL-extractable, but often overestimated; c) CAL-extractable P includes a fraction of CAT-extractable P.

Derived from these assumptions, the estimated plant-available P was modelled (P_{mod}) according to Equation (1).

Equation 1:

$$P_{mod} = P_{CAT} + (P_{CAL} - P_{CAT}) \times K_{CAL\text{-}CAT}$$

P_{CAT} = CAT-extractable amounts of P in the growing medium in mg pot^{-1}

P_{CAL} = CAL-extractable amounts of P in the growing medium in mg pot^{-1}

$K_{CAL\text{-}CAT}$ = Coefficient for plant-available CAL- but not CAT-soluble P in the growing medium

4. Sections

4.1. Section I

Summary

Phosphorus (P) is an essential nutrient for plant growth. In plant production, a sufficient P supply for plants is commonly provided by fertilization with rock phosphate (RockP)-based fertilizers. However, the RockP resources are finite and the worldwide reserves are located in only a few countries. To address this issue of P scarcity, the use of secondary P sources in crop production based on growing media may help to conserve the finite resources and mitigate the limited geopolitical accessibility. There is a lack of knowledge concerning the plant availability of secondary source-P being suitable for soilless crop production. In this light, a pot trial with 17 secondary P sources differing in terms of feedstock and processing (untreated, thermally or thermochemically treated, and precipitated) was conducted. Their P efficacy was tested and compared against water-soluble monocalcium phosphate (MCP) using marigold as P-sensitive model plant. In addition, the calcium chloride + diethylenetriaminepentaacetate (CAT) and/or calcium-acetate-lactate (CAL) extractable P amount in the growing medium at trial start (P_{CAT} and P_{CAL}, respectively) was tested to their suitability to reflect plant P uptake at trial end. After two weeks of cultivation, two out of 17 secondary P sources exhibited strong P deficiency symptoms (anthocyanosis and a reduction in plant growth) and for four additional products, the P uptake was reduced compared to the water-soluble reference fertilizer. After four weeks, at the end of the experiment, only three of the 17 tested secondary P sources (all precipitated struvite-forms) showed fertilizer efficacy comparable to MCP-P. The remaining sources showed P uptake ranging from 4% to 91% of MCP-P. Precipitates from liquid waste streams and untreated organic wastes, with the exception of sewage sludge and compost, had P uptake varying between 71% and 100%. The widest variability (4%–86%) was exhibited by thermally and thermochemically treated secondary P sources. A close relation between plant P uptake and P_{CAT} ($R^2 = 0.76$) and P_{CAL} ($R^2 = 0.78$), respectively, was observed. In addition, a combination of P_{CAT} and P_{CAL} improved the correlation ($R^2 = 0.89$). It can be concluded that most struvite-forms make a viable alternative to P-fertilizers derived from RockP providing base fertilization in growing media-based crop production. Furthermore, the new approach combing P_{CAT} and P_{CAL} offers high potential evaluating the plant availability of secondary source-P in soilless growing media.

Screening trial

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Dieter Lohr: Supervising laboratory analyses, and writing - review and editing.
Elke Meinken: Writing - review and editing, project administration, and funding acquisition.
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REGULAR ARTICLE

Availability of phosphorus recovered from waste streams to plants cultivated in soilless growing media

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Abstract

Background: Using secondary phosphorus (P) sources recovered from waste streams for base fertilization of soilless growing media may help conserve the global phosphate resources. However, little is known regarding the plant availability of P from secondary sources for soilless plant production.

Aim: The objective of this study was to investigate the plant availability of P from secondary sources using a peat-based growing medium and standard extraction methods.

Methods: Seventeen secondary P sources differing in terms of feedstock and processing were tested, and their fertilization efficacy was compared with that of water-soluble monocalcium phosphate (MCP-P) in a pot experiment using marigolds. The correlation of plant P uptake with calcium chloride + diethylenetriaminepentaacetate (CAT) and/or calcium–acetate–lactate (CAL) extractable P amount in the growing medium (P_{CAT} and P_{CAL}, respectively) was examined.

Results: Only three of the 17 tested secondary P sources (all struvite forms) exhibited comparable fertilization efficacy to MCP-P. The remaining sources showed P uptake varying between 4% and 91% of MCP-P. For precipitates from liquid waste streams and untreated organic waste, except for sewage sludge and compost, the P uptake ranged from 71% to 100%. The highest variability (4%–86%) was observed for thermally and thermochemically treated secondary P sources. Plant P uptake was closely correlated with P_{CAT} ($R^2 = 0.76$) and P_{CAL} ($R^2 = 0.78$), and this correlation became even stronger when P_{CAT} and P_{CAL} were combined ($R^2 = 0.89$).

Conclusions: Most struvite forms meet the requirements of base P fertilization for soilless plant production and can substitute water-soluble fertilizers obtained from primary P sources. The combination of P_{CAT} and P_{CAL} may be a promising approach to characterize the plant availability of P from secondary sources in soilless growing media and warrants further consideration.

KEYWORDS
fertilization, horticulture, phosphorus recycling, plant nutrition, plant production

1 | INTRODUCTION

Approximately 80% of the mined rock phosphate (RP) is used to produce fertilizers for agricultural purposes (Scholz et al., 2013). However, within the next few centuries, RP deposits will be exhausted (Dawson & Hilton, 2011; van Vuuren et al., 2010), but the demand for phosphorus (P) fertilizers for use in agriculture will increase to meet the requirement of food of the growing human population. Therefore, closing the P cycle in agriculture is crucial to ensure sustainable use of finite RP reserves (European Commission, 2015; Li et al., 2015; Moeller et al., 2018; Scholz & Wellmer, 2019). In this light, the on-farm use of P-rich waste, such as sewage sludge, animal manure, biogas digestate, or compost, as fertilizer for plant production can contribute to the closing of the P cycle. In Germany, the utilization of such P sources may fulfill up to 71% of the total national demand for P (Wiesler et al., 2020). However, the use of these P sources is often limited by their high transportation cost because of the relatively low content of P and the risk of exposure to contaminants, such as heavy metals and organic pollutants, or pathogens (Baize, 2009; Harrison et al., 2006; Magri et al., 2019). Nevertheless, these feedstocks have a high potential for P recycling (Ye et al., 2017), and several innovative technologies for P recovery from waste streams have been developed over the last decade (Kabbe et al., 2015). The current recovery technologies are based on either the precipitation of P from liquid waste (e.g., struvite), or the thermal (ash or biochar) and thermochemical (e.g., glown phosphates) treatment of solid wastes.

To establish such innovative recycled fertilizers for use in plant production, the plant availability of recovered P must be evaluated. Such evaluations have previously been performed through soil-based pot experiments and field trials of various agricultural crops (e.g., Appel & Friedrich, 2017; Lemming et al., 2017; Römer, 2006; Vogel et al., 2017; Wollmann et al., 2018), and there is scientific consensus on the use of recycled P for plant production in mineral soils (Huygens & Saveyn, 2018; Kratz et al., 2019; Moeller et al., 2018). Of note, the efficacy of recycled P fertilizers is an important factor. Precipitated struvite exhibits high plant availability, often comparable to water-soluble P fertilizers. However, the plant availability of P from thermally or thermochemically treated solid waste considerably varies depending on the type of feedstock, the process of P recycling, and pH of soil. For thermally treated (incinerated or pyrolyzed) feedstocks, higher process temperature can adversely affect the P availability of the resulting product due to increased crystallinity of P compounds (e.g., calcium phosphates) (Appel & Friedrich, 2017; Steckenmesser et al., 2019). To produce P compounds with high plant availability from high-temperature processes, additives, such as sodium salts, are used during incineration or further ash treatment (e.g., acid digestion) (Kratz et al., 2019).

In addition to soil-based plant production, several economically important cultivation systems use soilless growing media. These media consist mainly of peat and other organic materials such as wood fiber, green compost, or coir. In Germany, the annual production of soilless growing media reaches 8–9 million cubic meters (Schmilewski, 2017a, 2017b). The use of P from secondary sources for base fertilization may help conserve global RP resources. However, the dynamics of P in mineral soils and soilless growing media differ significantly (Khandan-Mirkohi & Schenk, 2008). The P buffering capacity of growing media is an important driver of P dynamics. As opposed to mineral soil, peat-based growing media nearly lack the buffering capacity for P (Khandan-Mirkohi & Schenk, 2008). Due to their negligible buffering capacity, P mobility is higher in growing media than in most mineral soils. As such, the P depletion zone around roots in growing media was approximately 10 times greater than that in mineral soils (Khandan-Mirkohi & Schenk, 2008). A resulting overlap of the depletion zones leads to higher spatial accessibility of P in soilless growing media.

Thus, the applicability of the current knowledge gained from work in soil-based systems to soilless production remains questionable, and only a few experiments using soilless growing media have been performed (Ehmann et al., 2019; Grunert et al., 2019; Hauck et al., 2021). Therefore, this topic was addressed in the present study.

Whether the common extractants used in Germany, namely calcium chloride + diethylenetriaminepentaacetate (CAT) or calcium–acetate–lactate (CAL), are suitable for characterizing the plant availability of P from secondary sources in soilless growing media remains unknown. The CAT method reflects readily soluble P, but underestimates the less soluble reserves (Alt et al., 1994). In contrast, the plant availability of CAL-extractable P is often overestimated, particularly when sparingly soluble calcium phosphates, which are the predominant P compounds in RP or composts (Frossard et al., 2002; García-Albacete et al., 2012), are applied or when the growing media are rich in clay and have high pH (Alt et al., 1994; Handreck, 1996).

To bridge the knowledge gap regarding the suitability of using recovered P for soilless production, a pot trial was conducted using marigold (*Tagetes patula* × *erecta*) as a P-sensitive model plant. Using a peat-based growing medium, 17 secondary P sources were tested, and their efficacy was compared to that of water-soluble monocalcium phosphate (MCP-P). CAT- and CAL-extractable amount of P (P_{CAT} and P_{CAL}, respectively) in fertilized growing media at the beginning of the experiment was determined, and its correlation with plant P uptake was examined. We hypothesized that (1) all secondary P sources can compete with water-soluble fertilizers for plant availability and (2) CAT and/or CAL are suitable extractants for assessing the plant availability of P from secondary sources.

2 | MATERIALS AND METHODS

2.1 | Tested secondary P sources and control fertilizer

Seventeen secondary P sources, including four thermally and three thermochemically treated solid wastes, five precipitates from two liquid waste streams (wastewater or manure), and five untreated feedstocks, were tested in the present experiment. The test sources were obtained according to the latest developments in their specific production methods (Table 1). Water-soluble MCP-P [$Ca(H_2PO_4)_2 \cdot H_2O$,

TABLE 1 Description of the secondary phosphorus sources tested, sorted by the type of feedstock treatment, and their chemical characterization according to the German fertilizer ordinance. Aqua regia soluble phosphorus (P) (P_{total}) is expressed in milligrams per gram of dry matter (DM), and water-soluble P (P_{H2O}), alkaline ammonium citrate-soluble P (P_{AAC}), and 2% formic acid-soluble P (P_{FA}) is expressed as the percentage of P_{total}

Description of the tested secondary phosphorus sources				Chemical characterization			
				P_{total}	P_{H2O}	P_{AAC}	P_{FA}
Group	ID	Brief information of the actual production process	Process reference	mg (g DM)$^{-1}$	Percentage of P_{total}		
Untreated	DG1	Dried, ground biogas digestate (manure, clover grass mix, and whole grain)	–	8.7	23	91	91
	DG2	Dried, ground biogas digestate (manure, clover grass mix, and corn crop mix)	–	16.1	34	80	97
	COM	Municipal greenwaste compost	–	3.1	10	100	94
	SDG	Ground, separated solid part of biogas digestate (slurry and corn and grain silage)	–	11.1	51	78	77
	SS	Dried sewage sludge from the municipal wastewater treatment plant in Klaerwerk II, Nuremberg, Germany	–	30.9	1	38	49
Thermally treated	SSA	Sewage sludge ash produced by monoincineration (800–900°C) at the wastewater treatment plant in Steinhäule, Neu-Ulm, Germany	–	67.0	0[a]	25	67
	BC–650	Biochar from sewage sludge (PYREG process at 650°C) produced at the wastewater treatment plant in Linz-Unkel, Linz, Germany	Appel and Friedrich (2017)	46.6	0[a]	17	11
	BC-SDG400	Biochar from biogas digestate SDG (TCR process, two-step pyrolysis at a treatment temperature of 400°C)	Stenzel et al. (2015)	22.8	5	83	86
	BC-SDG700	Biochar from biogas digestate SDG (TCR process, two-step pyrolysis at treatment temperatures 400 and 700°C)	Stenzel et al. (2015)	31.5	3	46	76
Thermochemically treated	ASHDEC	Melting fusion of sewage sludge with Na_2SO_4 at 950°C	Havukainen et al. (2016)	75.1	1	77	89
	MEPHREC-SS	Metallurgic gasification of sewage sludge SS with coke and lime at 1600°C	Hagspiel (2019)	19.1	0[a]	2	47
	SERAPLANT	Acid digestion of sewage sludge ash with H_3PO_4 (SERAPLANT technology based on the RecoPhos process)	Weigand et al. (2013)	158.8	51	97	78
Precipitated	PROC	Precipitation of calcium phosphates and struvite on the surface of calcium-silicate hydrate during wastewater processing	Berg et al. (2005)	40.4	2	86	100
	STR-AIRPREX	Struvite precipitation with $MgCl_2$ (AirPrex process) during wastewater processing at the treatment plant in Berlin, Germany	Kabbe et al. (2015)	103.8	3	14	100
	STR-STUTTGART	Struvite precipitation with MgO following acid digestion with H_2SO_4 (Stuttgart process) during wastewater processing	Krämer (2019)	102.4	6	13	100
	STR-GALV	Struvite precipitation from wastewater using a galvanic cell	Bilbao (2014)	97.3	0[a]	4	101
	STR-SLURRY	Precipitation of struvite and calcium phosphates from pig slurry using KOH/NaOH as flocculant	Bilbao (2017)	111.9	2	26	100

[a] < 0.5 soluble P as the percentage of P_{total}.

TABLE 2 Characterization of white peat used in the present study. The degree of degradation was classified according to the von Post scale (von Post, 1922), and particle size was expressed in millimeters (DIN, 2005). pH is indicated in $CaCl_2$; water-soluble salts are expressed in gram KCl per liter, and CAT-soluble N, P, and K are expressed in milligrams per liter according to VDLUFA (1991)

	Degree of degradation	Particle size	pH ($CaCl_2$)	Soluble salts (H_2O)	Soluble N (CAT)	Soluble P	Soluble K
White peat	H3–H5	< 8	3.1	0.10	17	0	8

Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany] was used as the control fertilizer.

2.2 | Growing medium

White peat (Table 2) was adjusted to pH 6.0 using Otterbein Naturkalk (85% $CaCO_3$; Zement- und Kalkwerke Otterbein, Großenlüder-Müs, Germany). A custom blended phosphate-free fertilizer (19–0–19 plus trace elements; Planta Düngemittel, Regenstauf, Germany) was used for base fertilization at the level of 200 mg N L^{-1}. The NH_4-N:NO_3-N ratio was approximately 1:3. To supplement the growing medium with P, fine powdery material of each source was carefully mixed, and then the solid secondary P sources or dissolved MCP-P were homogeneously mixed in individual growing medium portions, following standard horticultural practices. For each growing medium blend, the level of P fertilization was 70 mg P_{total} per liter, equivalent to 25 mg per pot. To ensure uniform P supply, the fertilized growing media were filled into pots by weight, immediately before the pricking of the marigold seedlings.

2.3 | Cultivation management and experimental design

Marigold ("Zenith Red F1"; Weigelt Samen, Grolsheim, Germany) seeds were sown in a peat-based growing medium and precultivated following conventional practices. On 02 July 2018, 2 weeks after sowing, seedlings were individually (one plant per pot) transferred into plastic pots (diameter, 10 cm; volume, 400 mL; Teku, Pöppelmann Kunststoff-Technik, Lohne, Germany). The pots were arranged into four replicates, each including 10 pots per treatment, using a completely randomized block design inside a greenhouse. Two of the 10 pots were used for analysis of the growing medium in weeks 1 and 3. From the rest of the eight pots, four were harvested in week 2 and the remaining in week 4. The greenhouse temperature was controlled at 22/20°C (day/night) for heating and 25°C for ventilation. Throughout the experiment, the plants were regularly supplied a P-free multi-nutrient fertilizer. This supply was adjusted according to the estimated nutrient demand through previous experiments and weekly analyses of the growing media (data not shown). As required, a dissolved fertilizer was supplied at a dose of 20 mg N per pot (once in week 2, two times in week 3, and three times in week 4 at maximum). Between fertilization events, the plants were irrigated as required with deionized water, following standard horticultural practices. To avoid nutrient loss through leaching, pots were placed into saucers, and the leachates were poured back into the pots. Additionally, the saucers were flushed back with deionized water before each harvest. To manage the mild infestation of thrips and leafminers, the insecticide Vertimec Pro (Syngenta Group, Basel, Switzerland) was applied three times at a concentration of 0.1%.

2.4 | Data collection

The plants were harvested at two time points: after 2 weeks of cultivation, to gain information on secondary P sources that led to insufficient P supply at very early stages of plant development, and after 4 weeks of cultivation, when 90% of the plants fertilized with MCP-P had reached the flowering stage. Per replicate, four pots of each treatment were pooled for the analysis of plants and growing medium. Plant dry weight was recorded after drying to a constant weight at 70°C in a forced-air oven. The dried plant material was ground to particles (< 0.5 mm) using a centrifugal mill (ZM1; Retsch, Haan, Germany), and acid digestion in a HNO_3:H_2O_2 mixture was performed under pressure in a microwave oven (Multiwave ECO; Anton Paar, Graz, Austria), according to the method described by Miller (1998). P in the digestion solution was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-OES) (iCap 6000 Dual View; Thermo Fisher Scientific, Dreieich, Germany), and plant P uptake was calculated by multiplying the P content by dry weight.

In the growing medium, P_{CAT} and P_{CAL} were analyzed according to the VDLUFA methods A 6.2.1.1 and 13.1.1 (VDLUFA, 1991) at the start and end of the trial, respectively. As described for plant analysis, P_{CAT} and P_{CAL} in the extract were determined using ICP-OES.

2.5 | Data analysis

Plant dry weight, P content, and P uptake at both harvest dates were subjected to one-way analysis of variance (ANOVA) using generalized linear modeling. When significant differences were noted, Dunnett test was used at a significance level of < 0.05 using MCP-P treatment as the control. The effects of processing on plant P availability were tested by separate comparisons of untreated and thermochemically treated sewage sludge (SS and MEPHREC-SS) as well as separated solid biogas digestate (SDG) and two types of biochar produced thereof (BC-SDG400 and BC-SDG700) using ANOVA, followed by Tukey's tests, with a significance level of < 0.05. The correlation between plant P

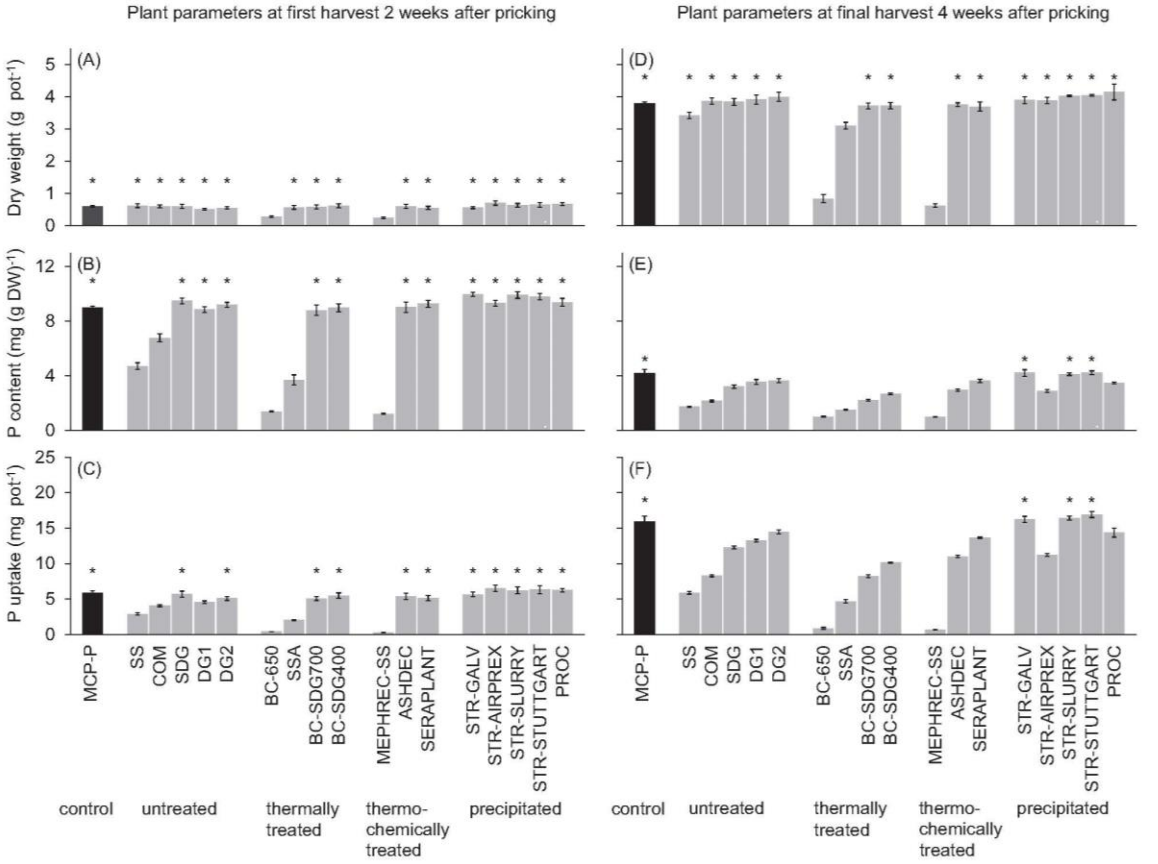

FIGURE 1 Dry weight (A, D), phosphorus (P) content (B, E), and P uptake (C, F) of marigold plants fertilized with secondary P sources (untreated and thermally or thermochemically treated solid feedstocks and precipitates from liquid waste streams) or water-soluble monocalcium phosphate (MCP-P) at 2 (A–C) and 4 (D–F) weeks after pricking. Details of the secondary P sources are summarized in Table 1. Treatments with asterisks are not significantly different from the MCP-P control (Dunnett test, $p < 0.05$). Error bars represent the standard error of mean ($n = 4$)

uptake and extractable P amount in the growing medium (P_{CAT} and P_{CAL} alone and in combination) was evaluated using regression analysis. ANOVA and post hoc tests were performed using Minitab V18 (Minitab Inc., State College PA, USA); regression analysis was performed using the least squares approach with the MS Excel SOLVER function (Hossain et al., 2013); and graphs were created with the *ggplot2* (Wickham, 2016) package in R v.4.0.2 (R Development Core Team, 2008).

3 | RESULTS

At the final harvest, the dry weight of plants fertilized with secondary P sources, except for SSA, BC-650, and MEPHREC-SS (Figure 1D), was comparable to that of control plants fertilized with MCP-P. Plants fertilized with BC-650 and MEPHREC-SS showed reduced growth, which was already evident in the second week of cultivation (Figure 1A), and this reduction further worsened over time. Compared with that of control plants fertilized with MCP-P, dry weight of plants fertilized with BC-650 and MEPHREC-SS was reduced by, respectively, 53% and 58% after 2 weeks of cultivation and by, respectively, 78% and 83% at the final harvest. Moreover, at the end of the experiment, dry weight of plants fertilized with SSA was 20% lower than that of control plants. This considerably reduced growth of plants fertilized with BC-650, and MEPHREC-SS was associated with significantly decreased P content, which was, respectively, 16% and 13% of the control value after 2 weeks of cultivation (Figure 1B). Plants fertilized with SSA, SS, and COM showed significantly decreased P content, which was, respectively, 33%, 55%, and 77% of the control value. At the final harvest, the P content of plants fertilized with STR-STUTTGART, STR-GALV, and STR-SLURRY was comparable to that of controls (Figure 1E). The result of statistical analysis of plant P uptake was identical to that of P content for all treatments, except for DG1 at the first harvest date (Figure 1C,F).

As shown in Figure 2A–C, dry weight, P content, and P uptake of plants fertilized with processed MEPHREC-SS were significantly reduced to, respectively, 18%, 57%, and 11% compared with the values of plants fertilized with the feedstock SS. Processed BC-SDG400 and

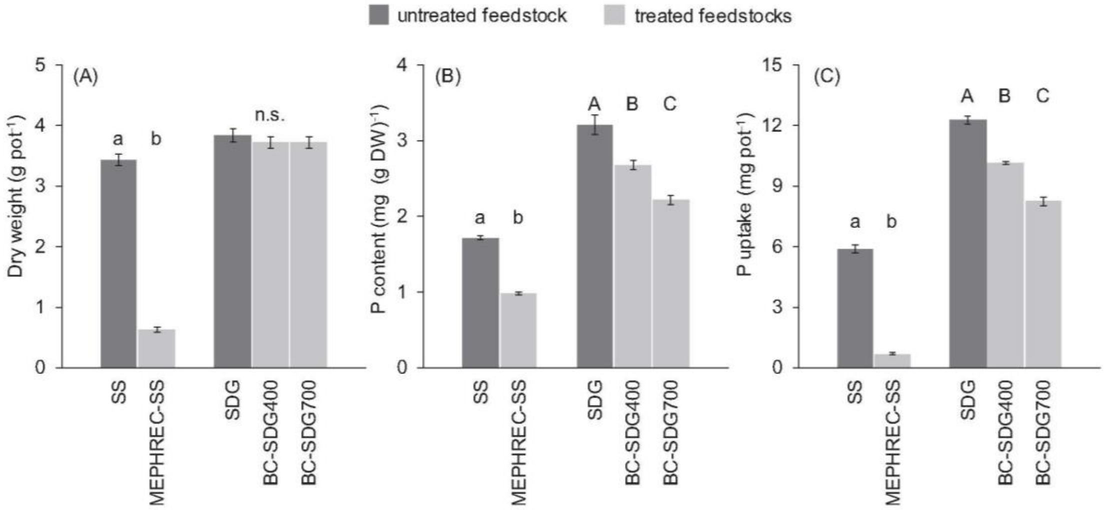

FIGURE 2 Dry weight (A), phosphorus (P) content (B), and P uptake (C) of marigold plants fertilized with processed secondary P sources (MEPHREC-SS, BC-SDG400, and BC-SDG700) and their feedstocks [SS and solid biogas digestate (SDG)] at the end of the trial. Different letters in lowercase indicate significant differences between SS and MEPHREC-SS and those in uppercase indicate significant differences among SDG, BC-SDG400, and BC-SDG700 (Tukey's test, $p < 0.05$). Error bars represent the standard error of mean ($n = 4$)

BC-SDG700 did not adversely affect dry weight of plants compared with their feedstock (SDG), although P content and P uptake were significantly reduced to 83% at 400°C, and to, respectively, 69% and 67% at 700°C pyrolysis temperature.

At the start of the experiment, P_{CAL} was consistently high (84–115% of applied P_{total}) in the growing media fertilized with precipitates from liquid waste streams. In contrast, there were large variations in P_{CAL}, ranging from 4 to 88% of applied P_{total}, in the growing media fertilized with untreated (36%–88% of P_{total}) and thermally (12–48% of P_{total}) or thermochemically (4–72% of P_{total}) treated solid waste, respectively. In contrast, P_{CAT} was consistently lower than P_{CAL}, and the correlation between P_{CAT} and P_{CAL} was relatively weak ($R^2 = 0.50$). While P_{CAT} was approximately fourfold lower than P_{CAL} for the growing media fertilized with PROC, STR-AIRPREX, and SS, it was over 75% of P_{CAL} for the growing media fertilized with DG1, SDG, STR-GALV, and STR-STUTTGART. The difference between P_{CAT} and P_{CAL} remained evident even at the end of the trial (Table 3).

After 4 weeks of cultivation, plant P uptake was closely correlated with P_{CAT} and P_{CAL} at the start of the trial ($R^2 = 0.76$ and 0.78, respectively) (Figure 3). However, the course of the regression lines did not correspond to the bisector. As shown in Figure 3A, the plant P uptake was underestimated when P_{CAT} was below 15 mg pot^{-1}, and this underestimation was negatively correlated with plant P uptake. In contrast, the plant P uptake was overestimated when P_{CAL} exeeds 5 mg pot^{-1}, and this overestimation was positively correlated to plant P uptake. In addition to these systematic differences, for some secondary P sources (PROC and STR-AIRPREX) the plant P uptake differs considerably from the calculated value using a simple regression model.

For all regression models combining P_{CAT} and P_{CAL}, the best fit for P uptake was obtained under the assumption that P soluble in CAT is entirely available, while P extractable by CAL but not by CAT is only partly available to plants, as expressed using Equation (1):

$$P_{mod} = P_{CAT} + (P_{CAL} - P_{CAT}) \times K_{CAL-CAT} \qquad (1)$$

where P_{mod} is estimated amount of plant-available P in the growing medium; P_{CAT} is amount of CAT-extractable P in the growing medium at the start of the trial (mg P pot^{-1}); P_{CAL} is amount of CAL-extractable P in the growing medium at the start of the trial (mg P pot^{-1}); and $K_{CAL\text{-}CAT}$ is percentage of P extractable by CAL but not by CAT in the growing medium at the start of the trial taken up by plants.

The amount of plant-available P estimated using Equation (1) matched well with the P uptake of plants (Figure 4). The coefficient of determination for the combination of P_{CAT} and P_{CAL} was significantly higher ($R^2 = 0.89$) than the individual coefficients for P_{CAT} and P_{CAL} (Figure 3), and there was no systematical under- or overestimation across the entire range of the estimated amount of plant-available P in the growing medium. The plant availability of P extractable by CAL but not by CAT was 30% ($K_{CAL\text{-}CAT} = 0.3$).

4 | DISCUSSION

4.1 | Plant availability of P from secondary sources

The plant availability of P from different secondary sources showed a very high variability. Among the four types of sources (untreated, thermally or thermochemically treated solid waste, and calcium or magnesium precipitates from liquid waste streams) P recovered from the precipitation showed the highest availability. As such, for three of the four tested struvite forms (STR-STUTTGART, STR-GALV, and STR-SLURRY), plant P uptake was comparable to the control value

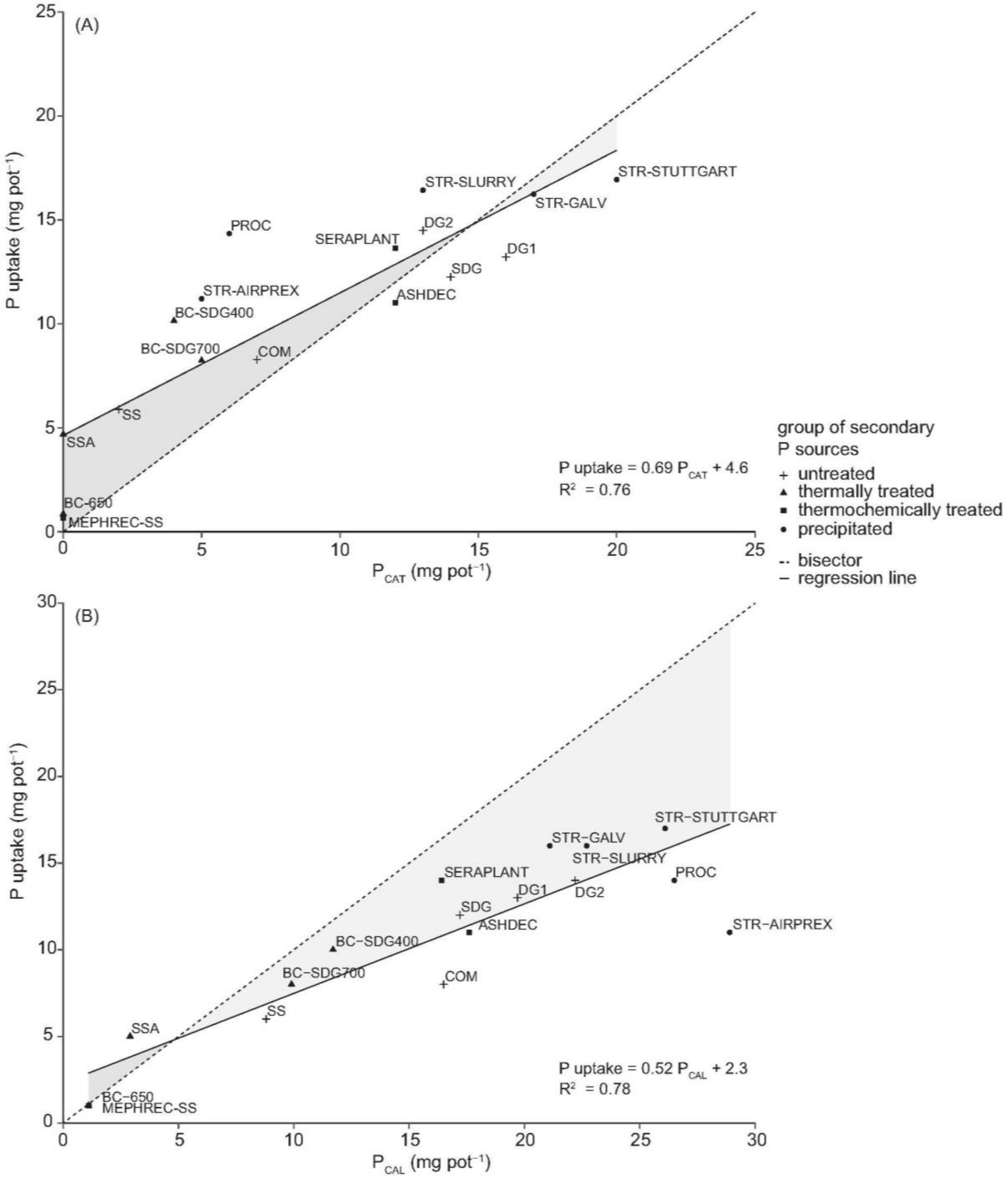

FIGURE 3 Correlation of the phosphorus (P) uptake of marigold plants at final harvest to P_{CAT} (A) and P_{CAL} (B) at the trial start in the growing media fertilized with secondary P sources. Dark gray shading highlights the underestimation and light gray shading highlights the overestimation of P uptake in the regression models

TABLE 3 CAT and CAL extractable amount of P (P_{CAT} and P_{CAL}, respectively) in the growing medium (mg pot^{-1}) fertilized with water-soluble MCP-P and secondary P sources (untreated and thermally or thermochemically treated solid feedstocks and precipitates from liquid waste streams) at the start and end of the experiment. Details of secondary P sources are summarized in Table 1. Values at the end of the experiment are presented as mean ± standard deviation ($n = 4$)

Secondary phosphorus sources		Trial start		Trial end	
Group	ID	P_{CAT}	P_{CAL}	P_{CAT}	P_{CAL}
Untreated	COM	6.8	16.5	1.9 ± 0.4	6.5 ± 0.2
	DG1	16.0	19.7	1.9 ± 0.2	4.0 ± 0.6
	DG2	12.8	22.2	1.4 ± 0.4	3.5 ± 1.7
	SDG	13.6	17.2	1.1 ± 0.4	2.4 ± 0.6
	SS	1.9	8.8	0.5 ± 0.1	5.5 ± 0.6
Thermally treated	BC650	0.1	1.1	0.2 ± 0.0	1.7 ± 1.5
	BC-SDG400	4.9	11.7	0.6 ± 0.2	3.0 ± 0.2
	BC-SDG700	3.9	9.9	0.4 ± 0.1	3.8 ± 1.6
	SSA	0.5	2.9	0.2 ± 0.1	2.4 ± 1.2
Thermochemically treated	ASHDEC	12.0	17.6	0.9 ± 0.1	4.1 ± 0.3
	MEPHREC-SS	0.0	1.1	0.1 ± 0.1	1.6 ± 1.4
	SERAPLANT	12.1	16.4	1.0 ± 0.2	5.1 ± 3.0
Precipitated	PROC	5.8	26.5	1.7 ± 0.3	8.0 ± 2.4
	STR-AIRPREX	5.2	28.9	3.0 ± 0.4	6.6 ± 2.6
	STR-GALV	17.5	21.1	1.9 ± 0.2	6.0 ± 2.2
	STR-SLURRY	13.1	22.7	1.7 ± 0.1	3.2 ± 1.5
	STR-STUTTGART	19.9	26.1	1.6 ± 0.1	3.7 ± 0.1
Control	MCP-P	16.4	n.a.	2.0 ± 0.4	6.4 ± 1.4

Abbreviation: n.a., not analyzed.

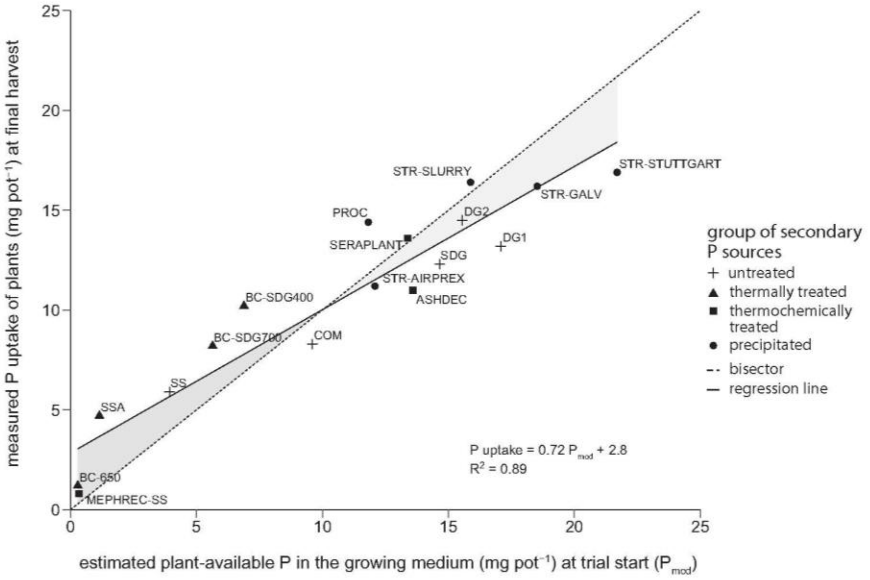

FIGURE 4 Correlation of the measured phosphorus (P) uptake of marigold plants at final harvest to the estimated amount of plant-available P (P_{mod}) in the growing media at the trial start based on P_{CAT} and P_{CAL}. Dark gray shading highlights the underestimation and light gray shading highlights the overestimation of P uptake in modeling

at the end of the trial. In contrast, plants fertilized with other secondary sources exhibited a significantly lower P uptake, in a range of 4% (MEPHREC-SS) to 91% (DG2). Therefore, the first hypothesis that all secondary P sources can compete with a water-soluble P fertilizer in soilless plant production was rejected.

The high plant availability of struvites has already been widely reported in trials using mineral soils (Kratz et al., 2019; Römer, 2013). Furthermore, our results for two of the struvites, namely STR-GALV and STR-SLURRY, are consistent with Ehmann et al. (2019) in similar pot trials with various ornamental plants. However, the P content and P uptake for one of the four struvites, STR-AIRPREX, were significantly reduced. This poor P availability of struvite derived from the AirPrex process is consistent with the findings of a previous soil-based pot experiment with maize (Wollmann et al., 2018). This result may be attributed to the insufficient standardization of the AirPrex process in terms of the initial composition of wastewater as well as pH and temperature in the precipitation reactor. As a result, the purity of struvite can be influenced by the formation of varying amounts of less available calcium phosphates instead of the readily available magnesium ammonium phosphate (Cabeza et al., 2011; Darwish et al., 2016; Muys et al., 2021). The presence of less available calcium phosphates explains also the slightly reduced P uptake of plants fertilized with PROC (Wollmann et al., 2018). The chemical structure of calcium phosphates in PROC can range from readily available brushite to poorly available hydroxyl apatite-like compounds (Penn & Camberato, 2019), and the plant availability of P is negatively correlated with both the degree of crystallization and the total P concentration (Berg et al., 2005). The P uptake of plants fertilized with PROC was approximately 90% of the control value, indicating that most of the calcium phosphates contained have a low degree of crystallization and thus a relatively high availability of P (Römer, 2006). This notion is further supported by the low total P concentration (8%) of the batch used in the present study (Berg et al., 2005).

Significant reductions in plant P content and P uptake, but not in dry weight, were noted for all untreated feedstocks at the end of the trial, corroborating the results reported by Ehmann et al. (2019). However, while the P uptake of plants fertilized with the tested biogas digestates reached at least 75% of the control value, for green waste compost and sewage sludge, P uptake was only 37% and 50% of the control value, respectively. In a pot trial with parsley, Link et al. (2015) observed similar P availability for several green and biowaste composts. The differences in the P uptake and P content of plants fertilized with biogas digestates and compost, respectively, were consistent with the percentage of water-soluble P relative to total P in these materials (23%, 34%, and 51% for the biogas digestates DG1, DG2, and SDG, respectively and only 10% for compost; Table 1). A possible reason for the low amount of water-soluble P and poor plant availability is the shift from organic P fractions to inorganic calcium phosphates and their subsequent aging during composting (Frossard et al., 2002; Peperzak et al., 1959). However, low plant availability of P is advantageous if composts or solid biogas digestates are not used as P fertilizer but as peat substitute in growing media up to 40% by volume (Schmitz & Meinken, 2009). The low availability of P from sewage sludge may be attributed to the high proportion of iron and aluminum phosphates (Lemming et al., 2020; Römer, 2006; Steckenmesser et al., 2019). This assumption is supported by the relatively low solubility of 49% of the total P in formic acid (Kratz et al., 2019).

Within the groups of thermally and thermochemically treated feedstocks, the fertilization efficacy was highly variable. Dry weight for one product per group (BC-650 and MEPHREC-SS) was already significantly reduced after 2 weeks of cultivation compared with the control value, dropping to only 22% for BC-650 and 17% for MEPHREC-SS after 4 weeks of cultivation. After 4 weeks, the dry weight of plants fertilized with the remaining five products ranged between 82% of the control for SSA and 95%–99% of the control for BC-SDG400, BC-SDG700, ASHDEC, and SERAPLANT. Only the difference between SSA and control was statistically significant. Relatively poor P availability from MEPHREC-SS, being significantly lower than that of the feedstock SS (Figure 2), has also been reported previously (Hagspiel, 2019; Kratz et al., 2019). This result may be attributed to very strong sintering during the metallurgical process at approximately 1200°C, which results in the formation of a vitreous structure (Hagspiel, 2019). In addition, the low P availability from sludge-based biochar (BC-650) can be explained by the high percentage of barely available iron and aluminum phosphates in the feedstock and a significant decrease in the availability of calcium phosphates during carbonization (Appel & Friedrich, 2017; Steckenmesser et al., 2017). This negative impact of carbonization was also evident from the comparison of P content and P uptake between SDG and the two biochars (BC-SDG400 and BC-SDG700) produced thereof (Figure 2). The decrease in P availability with the increase in carbonization temperature is well documented (Kratz et al., 2019). Indeed, the relatively good P availability from the two thermochemical products ASHDEC and SERAPLANT (Figure 1), despite process temperatures above 900°C, conflicts with these observations; however, for ASHDEC, the addition of sodium sulfate during the sintering process and the subsequent formation of readily available $CaNaPO_4$ (buchwaldite) is reasonable (Hermann & Schaaf, 2019; Stemann et al., 2015). The contrasting low P availability from ASHDEC described by Wollmann et al. (2018) can be explained by the use of magnesium chloride as an additive instead of sodium sulfate as in the present study, resulting in the formation of P-bearing phases with lower plant availability (Steckenmesser et al., 2017). In the case of SERAPLANT, its classification as a thermochemically treated secondary P source is questionable. In fact, it is sewage sludge ash, posttreated with phosphoric acid, analogous to the production of triple superphosphate (TSP) from RP as primary P source (Weigand et al., 2013). However, with respect to its remarkably high total P content of 15.9%, which is two times the average content of municipal and industrial sewage sludge ash (Krüger & Adam, 2015), and the fact that only 50% of the total P was water soluble compared to >90% for TSP, the rather high P availability may be caused by phosphoric acid itself rather than the digestion of the material.

4.2 | Correlation between plant P uptake and extractable P amount in the growing medium

For plant P uptake, the P concentration in the soil solution is highly relevant. In contrast to mineral soils, in peat-based growing media, this concentration depends almost exclusively on the chemical equilibrium constant of the P compounds contained in the fertilizers. The release of sorbed P into the solution is negligible, since peat has a low anion exchange capacity (Khandan-Mirkohi & Schenk, 2008). In this light, a growing medium extractant suitable to predict plant P uptake must reflect the concentration of dissolved P, and ideally, the amount of the extracted P corresponds to plant P uptake. Both extractants used in Germany, namely CAT and CAL, met the first requirement due to a high coefficient of determination between extractable P in the growing medium and plant P uptake (CAT: $R^2 = 0.76$; CAL: $R^2 = 0.78$). Thus, hypothesis 2 is confirmed for both extractants only at the first glance. Systematically, P_{CAT} was lower and P_{CAL} higher than plant P uptake. Therefore, not all requirements for an extractant assessing the plant availability of P are fulfilled.

As previously discussed, secondary P sources include a wide range of chemical structures accounting for great differences in plant availability. Magnesium ammonium phosphate and monocalcium phosphate are easily available, whereas di- and tri-calcium phosphates are less available (Römer, 2013) and apatite-like compounds are only available to some N_2-fixing legumes (Hauter & Steffens, 1985). According to Alt and Peters (1992), CAT extracts only the readily available phosphates, but not calcium phosphates with higher crystallinity. This explains the underestimation of plant P uptake from, for example, PROC and STR-AIRPREX, which contain abundant di-calcium phosphates, using CAT as the extractant (Berg et al., 2005; Kern et al., 2008; Muys et al., 2021). In contrast, due to the acidic and strongly buffered pH (pH 4.1), CAL overestimates plant P uptake from secondary sources containing abundant highly crystalline calcium phosphates (Alt et al., 1994), such as, for example, COM (Frossard et al., 2002). These disadvantages may be overcome using the proposed approach to predict plant P uptake from secondary P sources in peat-based growing media (Figure 4), based on the assumption that P extractable by CAT is completely plant-available, but P extractable by CAL, while not by CAT is only 30% plant-available ($K_{CAL\text{-}CAT} = 0.3$). Typically, however, this value of $K_{CAL\text{-}CAT}$ is not constant, as plant P uptake is affected by several factors. Specifically, P uptake efficiency is highly species-specific (Khandan-Mirkohi & Schenk, 2009), and plant P uptake closely depends on the pH of the growing medium (Hauck et al., 2021). Furthermore, P uptake is affected by the anion buffering capacity of the growing medium, grain size of the fertilizer, and environmental conditions (Khandan-Mirkohi & Schenk, 2009; Müller-Stöver et al., 2021). In further research, the effects of these factors on the value of $K_{CAL\text{-}CAT}$ must be addressed to validate the proposed approach.

5 | CONCLUSIONS

The plant availability of P from the secondary sources was highly variable. The P uptake by plants fertilized with secondary P sources ranged between 4% and 100% of that of the control plants fertilized with water-soluble MCP-P. For the base fertilization of growing media in soilless plant production, three precipitates from liquid waste streams (STR-GALV, STR-SLURRY, and STR-STUTTGART) may be promising substitutes for water-soluble fertilizers based on RP. Despite a close correlation of plant P uptake with P_{CAL} and P_{CAT} in the growing medium, none of the extractants was suitable for assessing the amount of plant-available P when used alone. However, the combination of P_{CAT} and P_{CAL} appears to be an approach worth pursuing.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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4.2. Section II

Summary

Secondary P sources may help conserve dwindling reserves of primary P (rock phosphate) by substituting primary P-derived fertilizers of high plant availability in crop production. In crops produced in growing media with a typical pH of approximately 6, the ability of secondary P sources to substitute primary P varied greatly, depending on the exhibited plant availability. According to common knowledge, plant availability of P fertilizers can differ among contrasting pH levels, which is attributed to P compounds' pH driven solubility. Besides growing media pH values of around 6, which fits the needs of most horticultural crops, acidophilic plant species such as *Azalea* ssp. require lower pH levels (pH < 5). In this light, this sections covers the effect of contrasting pH in the growing medium on secondary P sources' plant availability. In addition, the suitability of the new approach combing CAT- and CAL-extractable P in the growing medium (P_{mod}, section I) to reflect the plant availability of secondary sources-P in soilless growing media of contrasting pH is discussed. The stated section aims were investigated in three plant trials (pH trial 1, pH trial 2, SSA comparison) using different secondary P sources, and water-soluble monocalcium phosphate (MCP) and rock phosphate (RockP) as benchmark. In the pH trial 1, growing media preparation and pot filling was performed by volume according to horticultural practice. As secondary P sources, a thermally ($SSA_{Trollins1}$) and thermochemically treated sewage sludge (MEPHREC-SS), as well as precipitated struvite (STR-AIRPREX) derived from wastewater processing was used to fertilize growing media of contrasting pH (4.5–5.0, 5.5–6.0). Fertilization revealed different P plant availability among the different secondary p sources. After six weeks of cultivation ranking of plant dry weight at pH 4.5–5.0 was MCP = STR-AIRPREX = $SSA_{Trollins1}$ = RockP ≫ MEPHREC-SS and the ranking at pH 5.5–6.0 was MCP = STR-AIRPREX > $SSA_{Trollins1}$ = RockP > MEPHREC-SS. The ranking of plant P uptake was STR-AIRPREX > MCP > $SSA_{Trollins1}$ = RockP > MEPHREC-SS at pH 4.5-5.5 and STR-AIRPREX > MCP > $SSA_{Trollins1}$ = RockP > MEPHREC-SS at pH 5.5–6.0. Plant P availability of $SSA_{Trollins1}$ and RockP significantly increased under acidic conditions in the growing medium. None of the tested extractions methods (CAL-method, CAT-method) was able to reflect plant P uptake under growing medium pH <5 of $SSA_{Trollins1}$ and RockP, respectively.

In contrast to the pH trial 1, in pH trial 2, the growing media preparation and pot filling was performed more accurately by weight compared to the volume-based executions. In addition, three more secondary P sources were investigated: one digest (DG1), and two biochars (BC-650, BC-SDG400). At pH 6.0 in the growing medium $SSA_{Trollins1}$, BC-650, and MEPHREC-SS led to a lower fresh weight compared to MCP (28.2 g pot^{-1}), and in cases for BC-650 and MEPHREC-SS also lower values compared to the hardly plant-available RockP (12.3 g pot^{-1}) were observed. Considering P taken up by plants, no secondary P source could compete with plant P uptake derived from MCP (16.1 mg pot^{-1}), while only for plants fertilized with BC-650 and MEPHREC-SS lower values in P uptake was found compared to RockP (2.4 mg pot^{-1}). For the pH 4.5, higher plant P availability was observed for secondary P sources and the RockP control. Only for BC-650 and MEPHREC-SS fresh weight was less compared to the controls MCP (28.2 g pot^{-1}) and RockP (28.1 g pot^{-1}), respectively. However, considering P taken up by plants, no secondary P source led to a level similar to MCP (17.4 mg pot^{-1}). Compared to plant P uptake derived by RockP (12.6 mg pot^{-1}), only BC-650 and MEPHREC-SS values were much lower, while for the remaining secondary P sources slightly lower, comparable, or higher values were observed (10.9–15.5 mg pot^{-1}). The higher plant availability at growing medium pH 4.5 compared to pH 6.0, subsequently resulted in a higher relative P use efficiency (rPUE) of secondary source-P under acidic conditions in the growing medium. However, this enhancement in rPUE varied among the secondary P sources. While for BC-650 and MEPHREC-SS this enhancement was negligible low (<2 percentage points) and of no practical relevance for plant production, significant higher values were observed for the remaining secondary P sources (12–27 percentage points). Among the secondary P sources, $SSA_{Trollins1}$ exhibited the significantly highest enhancement.

The pH level in the growing medium also influenced the amounts of extractable P by CAT (P_{CAT}) and CAL (P_{CAL}). At a pH of 4.5, the extractable amounts of P were constantly higher compared to pH 6.0. This was less obvious for P_{CAL} than for P_{CAT}. At the trials start, P_{CAT} and P_{CAL} were strongly correlated ($R^2 > 0.76$) to P taken up by plants at the trials end. However none of the solvents was able to reflect the enhanced plant P availability of $SSA_{Trollins1}$ at a pH of 4.5 in the growing medium, and for P_{CAL} a strong overestimation of plant P uptake of STR-AIRPREX and DG1 was observed. For the new approach combining P_{CAT} and P_{CAL} the numerically best fit for plant P uptake ($R^2 = 0.83$) was observed. However, P_{CAT} and P_{mod} was strongly related ($R^2 > 0.99$) and thus P_{mod} did not significantly improve the prediction accuracy of plant-available secondary source-P.

According to the result obtained from previous trials, cultivation under acidic conditions in the growing medium was for $SSA_{Trollins1}$`s plant P availability the most beneficial. To proof if this observation can be generalized across different SSAs, a pot trial (SSA comparison) with six different SSAs ($SSA_{Trollins}$ batches 1–3, SSA_{Ostrau}, SSA_{Luenen}, $SSA_{Grosslappen}$) was conducted in growing media under contrasting pH (4.5, 6.0), and their fertilizer efficacy was benchmarked with MCP and RockP. At pH of 6.0 in the growing medium, no SSA reached the rPUE observed for MCP. However, at a growing medium pH of 4.5, plant availability of SSA-P increased and the average rPUE for SSA-P was 70% of the MCP value. Compared to plant availability of RockP-P, at a growing medium pH of 6.0, SSA-P resulted in an rPUE of nearly the same low level. In contrast, at pH 4.5, the rPUE of SSA-P was mostly lower than that from RockP-P, and there were differences in rPUE among SSAs. According to the data, these observed differences might be attributed to differences in the P-bearing phase of SSA, and to a variation in particle size distribution. The CAT- and CAL-based-growing media analyses, on their own or in combination, were not suitable to reflect plant P uptake from SSA-P. To predict plant-available SSA-P, solvent modifications or additional extractants might help to satisfactorily describe plant-available SSA-P.

pH trial 1

Hauck, D., Lohr, D., Meinken, E., and Schmidhalter, U. (2021). Plant availability of secondary phosphates depending on pH in a peat-based growing medium. *Acta Horticulturae, 1317,* 207-214.

Authors contribution:

Daniel Hauck: Conceptualization, Methodology, investigation, formal analysis, visualization, and writing - original draft preparation.

Dieter Lohr: Supervising laboratory analyses, and writing - review and editing.

Elke Meinken: Writing - review and editing, project administration, and funding acquisition.

Urs Schmidhalter: Review and editing, and supervision.

Plant availability of secondary phosphates depending on pH in a peat-based growing medium

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Abstract

Phosphorus (P) fertilizer consumption will deplete global reserves of rock phosphate within the next few centuries. Several technologies have been developed within the last decade to recover phosphate from P-rich waste streams. Recycling P fertilizers (secondary phosphates) is gaining increasing interest but little is known about the possible use of such products in soilless plant production systems. In this study, a greenhouse experiment with *Tagetes patula* x *T. erecta* 'F1 Zenith Red' as P sensitive model plant was conducted to determine the plant availability of three secondary phosphates: precipitated magnesia ammonium phosphate (Struvite), sewage sludge ash (SSA) and metallurgic granulate (Mephrec). Water soluble monocalcium phosphate (CaP) and rock phosphate (rock-P) were included as controls. The growing medium was peat limed to two pH levels (4.5-5.0, 5.5-6.0). Calcium chloride/DTPA (CAT) and calcium-acetate-lactate (CAL) soluble P was extracted at the beginning of the experiment to test if these solvents were suitable to predict plant availability of the P fertilizers. After 6 weeks of cultivation, dry matter and P uptake of the plants were determined. Ranking of dry weight at pH 4.5-5.5 was CaP = Struvite = SSA = rock-P ≫ Mephrec and at pH 5.5-6.0 CaP = Struvite > SSA > rock-P > Mephrec. Ranking of plant P uptake was Struvite > CaP > SSA = rock-P ≫ Mephrec at pH 4.5-5.5 and Struvite > CaP ≫ SSA = rock-P > Mephrec at pH 5.5-6.0. Among plants fertilized with SSA or rock-P, a significant increase in dry weight and P uptake was found by decreasing the pH from 5.5-6.0 to 4.5-5.5 in the growing medium. In comparison to CAL, CAT extracted a slightly lower amount of P from the growing medium. Neither CAT nor CAL was able to predict the increased P uptake from SSA and rock-P at pH 4.5-5.0.

Keywords: circular economy, fertilization, waste streams, ornamentals

INTRODUCTION

About 80 % of the mined rock phosphate is used in the fertilizer industry for agricultural purposes (Scholz et al., 2013). However, deposits of rock phosphate will be exhausted within the next few centuries (Dawson and Hilton, 2011; Mogollón et al., 2018). For a sustainable use of the finite resource of rock phosphate, closing phosphorus (P) cycles in agriculture and horticulture are a crucial need (Li et al., 2015; Möller et al., 2018). Phosphorus-rich wastes like sewage sludge, animal manure, biogas digestate or compost offer a high potential for P recycling (Ye et al., 2017). In this context, several innovative technologies for P-recovering from such wastes have been developed within the last decade (Kabbe et al., 2015; Ye et al., 2017). Whereas plant availability of secondary phosphates (sec-P) has received large attention in mineral soils (Nanzer et al., 2014; Wollmann et al., 2018; Wollmann and Möller, 2018), studies in soilless plant production systems are scarce (Ehmann et al., 2019).

The analysis of plant available phosphorus in growing media is crucial for optimizing fertilization. Alt and Peters (1992) introduced CAT as a suitable extractant for this purpose because nutrients are extracted near the actual pH of the growing medium. Compared to stronger extractants like CAL, which is buffered at pH 4.1, plant availability is not overestimated especially in growing media with high pH (Alt et al., 1994; Handreck, 1996). Whether these extractants are suitable to characterize plant availability of sec-P is not known.

For the assessment of several sec-P sources, a pot trial with *Tagetes* as a model plant in a soilless plant production system was conducted. The aims of this study were (i) to compare the fertilizing effect of sec-P produced by different technologies, (ii) to evaluate the effect of the pH in the growing medium on the plant availability of sec-P and (iii) to compare the suitability of the growing media extractants CAT and CAL to predict the plant availability of sec-P.

MATERIAL AND METHODS

Secondary phosphates and control fertilizers

The following three secondary phosphates were chosen as P fertilizers.

Struvite is precipitated magnesia ammonium phosphate from the municipal waste water treatment plant in Berlin, produced according to AirPrex® procedure.

Sewage sludge ash (SSA) is produced by mono incineration (~800 °C) of sewage sludge from the waste water treatment plant Steinhäule near Ulm city.

Mephrec is produced by the Mephrec® gasification process (1200 °C) using sewage sludge, lime and coke in a model reactor of the waste water treatment plant in Nuremberg.

Finely ground rock phosphate (rock-P) as a non-processed P fertilizer and water soluble monocalcium phosphate (CaP) as a highly processed P fertilizer made out of rock phosphate were used as control fertilizers.

Growing medium

The growing medium of the pot trial consisted of white peat (< 8 mm). A multinutrient fertilizer (19-0-15) including trace elements was used for basic fertilization at a level of 200 mg N L^{-1}. The NH_4-N : NO_3-N ratio was approximately 1:3. The fertilized peat was separated into two parts which were treated with different amounts of lime (3 or 5 g calcium carbonate L^{-1}) to reach a lower pH level of 4.5-5.0 and a higher pH level of 5.5-6.0. After liming, P fertilizers were applied to the mixtures based on 71 mg aqua regia extractable P L^{-1} which corresponds to approximately 25 mg P pot^{-1}.

Cultivation management and experimental design

Tagetes patula x *T. erecta* 'F1 Zenith Red' (Floranova) as a P sensitive model plant was cultivated in plastic pots (diameter 10 cm, volume 400 mL). Two weeks after sowing young plants were transplanted on October 22, 2018 into these pots and cultivated for 6 weeks in a greenhouse. Temperature of the greenhouse was set up to 20/18 °C (day/night) for heating and 23 °C for ventilation. Pots were placed into saucers to collect leachate. When leachate occurred it was swiftly recycled into the pot. Deionized water was used for irrigation. Every two weeks two pots of each treatment and replication were removed from the trial to analyze the CAT-soluble nutrient content in the growing medium. Based on these results plants were fertilized with N, K, Mg and micronutrients. Pots were arranged as a two factorial block design (four replications with 12 pots each).

Data collection

At the start of the experiment the soluble P content of the growing media was analyzed by using CAL and CAT as extractants according to methods A 6.2.1.1 and 13.1.1 of VDLUFA method book I (2012, 2004). At harvest the fresh shoot biomass was determined by pooling the remaining eight plants of each replication. After drying the plant material at 70 °C till constant weight the dry weight was recorded and the dried plants were milled < 0.5 mm using a centrifugal mill (Retsch ZM1, Retsch GmbH, Haan, Germany). To analyze the P content of the milled plant material an acid digestion (HNO_3/H_2O_2) in a microwave oven (Multiwave ECO, Anton Paar GmbH, Graz, Austria) was performed. The P determination in the extraction/digestion solutions was done by using an ICP-OES (iCapTM 6500 dual view, Thermo Fisher Scientific Inc., Waltham, United States). Phosphorus uptake of the plants was calculated by multiplication of P content and dry weight.

Statistical analysis

For statistical analysis Minitab V16 (Minitab Inc., State College PA) was used. An ANOVA was performed for dry weight and P uptake using the two factorial GLM-function model followed by a Tukey test and for P contents in the growing medium fertilizer specific ANOVA was calculated using the two factorial GLM-function model followed by a Tukey test.

RESULTS AND DISCUSSION

Plant performance of *Tagetes*

Tagetes plants fertilized with Struvite showed at both pH levels a dry matter production of about 4 g pot^{-1} which was comparable to plants fertilized with water soluble CaP (Figure 1). In contrast, with the cinder product Mephrec plant growth was the lowest. The dry weight of < 0.3 g pot^{-1} was even lower than in the rock-P control and the plants showed strong P deficiency symptoms. Under acidic conditions a positive effect on plant availability is known for natural apatites (Kanabo and Gilkes, 1987; Bolan and Hedley, 1990). This was clearly visible when rock-P was applied. This effect did not occur in the Mephrec treatment. Fertilization with SSA at pH 5.5-6.0 in the growing medium resulted in less dry weight (1.5 g pot^{-1}) than for Struvite or CaP. Here the performance of plants fertilized with SSA was comparable to those fertilized with rock-P. At pH 4.5-5.5 the SSA fertilized plants showed a higher dry weight of 3.8 g pot^{-1} which was equal to the CaP control. The observation that plants fertilized with SSA being cultivated under acidic conditions showed an increased yield is in accordance with Nanzer et al. (2014). They stated that the yield of *Lolium multiflorum* cultivated in a mineral soil fertilized with different SSAs also increases with decreasing pH of the soil.

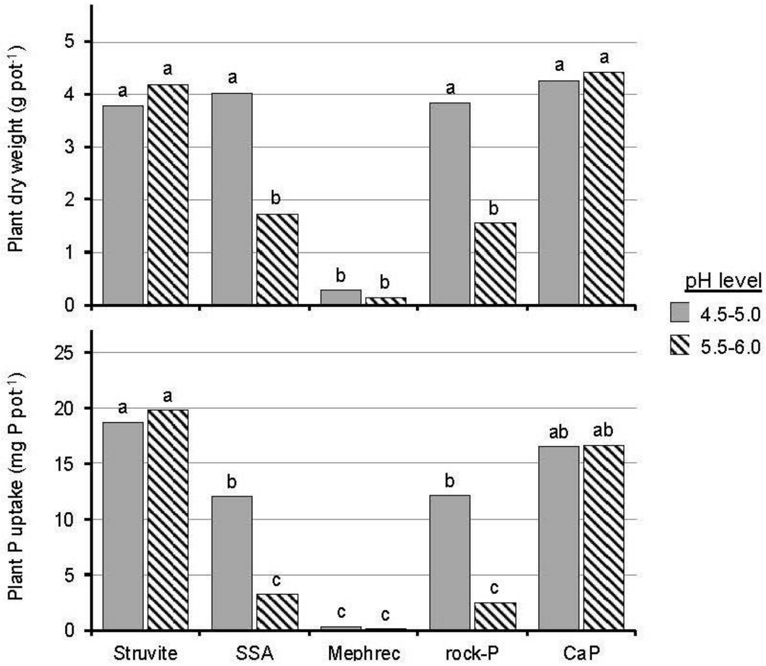

Figure 1: Dry weight and P uptake of *Tagetes* after six weeks of cultivation using one of five different P sources including struvite (Struvite), sewage sludge ash (SSA), metallurgic granulate (Mephrec), rock phosphorus (rock-P), and calcium phosphate (CaP). Different letters indicate significant difference between the treatments, Tukey test, $p < 0.05$.

P uptake of *Tagetes*

The differences in P uptake (Figure 1) are broadly consistent with those in dry weight production. Fertilization with Struvite resulted in a P uptake comparable to fertilization with CaP at both pH levels. Ehmann et al. (2019) also found that the P uptake of Chinese cabbage and *Tagetes* cultivated in a peat/clay mixture was the same for plants fertilized with Struvite and water soluble triple superphosphate, respectively. On the other hand the P uptake of sunflower was significantly lower from Struvite compared to water soluble triple superphosphate. Wollmann et al. (2018) reported for maize cultivated in a mineral soil a comparable P uptake from Struvite produced by the Stuttgarter® process and water soluble $Ca(H_2PO_4)_2$, while Struvite produced by the AirPrex@ procedure led in contrast to our results to a significant lower P uptake. The partly contradictory results might be due to different abilities of plants species in P uptake as well as different characteristics of crystallinity and purity of the Struvites themselves which may be caused by the various precipitation methods to produce Struvites from liquid P-rich waste streams.

CAT and CAL extractable phosphate in the growing medium

In the growing medium fertilized with Struvite and CaP, respectively, high amounts of P (> 52 mg P L^{-1}) were extractable. In contrast, much less P could be extracted from SSA, Mephrec and rock-P (Figure 2). CAL extracted more P than CAT in growing media fertilized with Struvite, SSA rock-P and Mephrec.

The higher pH level of the growing medium resulted for Struvite, SSA and rock-P in a significant decrease of extractable P regardless of the extracting agent. This is contrasting our expectations in the case of CAL because this extractant is strongly buffered at pH 4.1. As found for CaP the same value was expected for both pH levels. The pH effect on the CAT extractable P can be explained by the fact that the extraction occurs more or less at the actual pH of the growing medium (Alt et al., 1994). The slightly higher amounts of extractable P at higher pH level in the growing medium fertilized with Mephrec might be caused by the presence of Fe and Al phosphates.

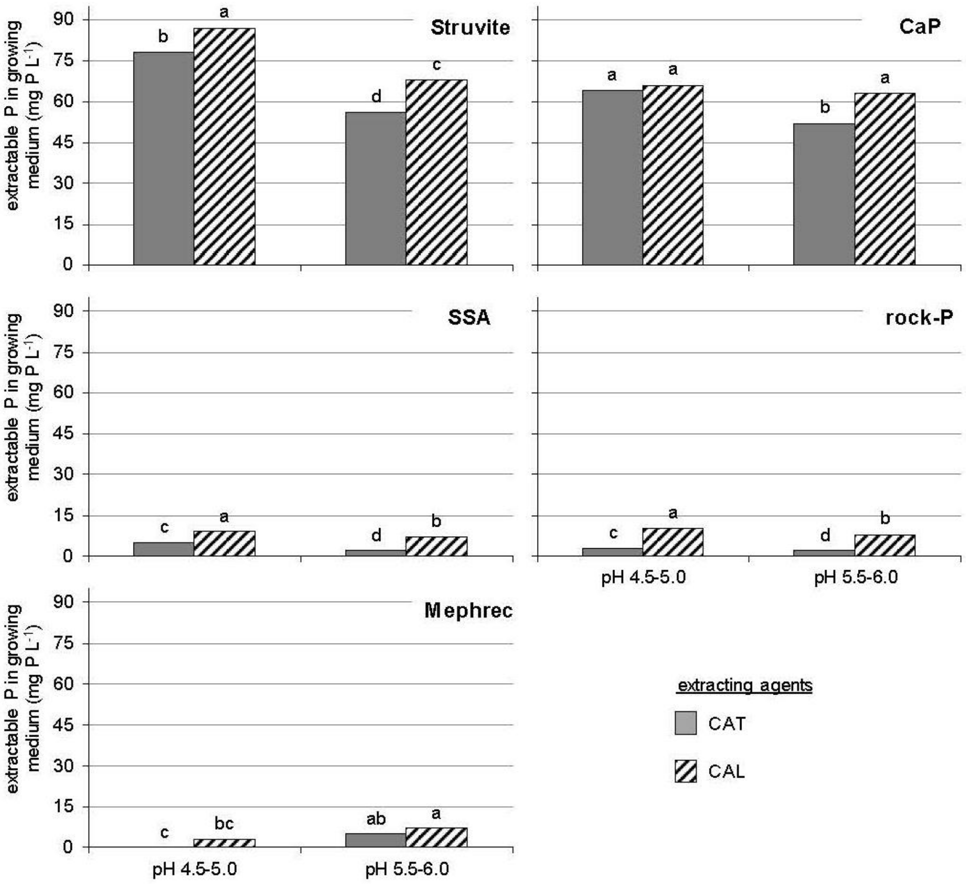

Figure 2: CAT and CAL extractable P of the growing medium fertilized with five different P sources including struvite (Struvite), sewage sludge ash (SSA), metallurgic granulate (Mephrec), rock phosphorus (rock-P), and calcium phosphate (CaP) at the start of the trial. Different letters indicate significant difference between the treatments, Tukey test, $p < 0.05$.

The results of the P analysis of the growing medium are nearly the same for SSA, Mephrec and rock-P (Figure 2). In contrast, plants dry weight and P uptake differ considerably (Figure 1). Therefore, neither CAT nor CAL could predict the plant availability of these secondary phosphates.

CONCLUSION

Plant availability of sec-P produced by different technologies largely differs. Cultivating at pH levels of < 5 in the growing medium can improve plant performance and P uptake for some products. Neither CAT nor CAL are suitable extractants to predict the plant availability of sec-P containing P compounds of low solubility.

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pH trial 2

The pH trial 2 contains results of an unpublished, highly standardized pH-trial with additional secondary P sources compared to pretrial pH trial 1. The aim of this study was to examine plant P availability of secondary P sources under contrasting pH (4.5, 6.0) in the growing medium. Secondary P sources were selected based on: (i) the expected effect on short term P availability for plants under acidic conditions in the growing medium (pretrial), and (ii) the leftover quantities from previous trials. In addition, it was investigated if the new approach estimating plant available P in growing media can reflect the plant availability of secondary P sources under contrasting pH in the growing medium.

Material and methods

Secondary P sources and control

The secondary P sources DG1, $SSA_{Trollins1}$, BC-650, BC-SDG400, MEPHREC-SS and STR-AIRPREX were investigated in this study.
As control fertilizers, water-soluble MCP ($Ca(H_2PO_4)_2 \cdot H_2O$, Sigma–Aldrich Chemie GmbH, Taufkirchen, Germany) and finely ground RockP (Hyperphos, producer unknown) were used.

Growing medium

White peat was used as the growing medium. The peat was split into two equal parts and limed to pH 4.5 (typical for acidophil plants, such as azalea) and 6.0 (typical for most ornamental plants) using Otterbein Naturkalk (85% CaCO3, Zement- und Kalkwerke Otterbein GmbH und Co. KG, Großenlueder-Mues, Germany). After liming, a P-free multinutrient fertilizer (19-0-15) with trace elements (custom blend, Planta Duengemittel GmbH, Regenstauf, Germany) was dissolved for base fertilization in deionized water and evenly mixed into the peat at a level of 200 mg N L^{-1}. After base fertilization, the secondary P sources and the control fertilizers were homogeneously mixed into individual growing medium portions at 70 mg aqua regia extractable P L^{-1} (equivalent to 25 mg P pot^{-1}). Secondary P sources and RockP were applied in solid form, whereas fully water-soluble MCP was provided as a solution. To ensure equal amounts of P per pot, the growing medium was filled into the pots by weight immediately before transplanting the precultivated marigold seedlings.

Cultivation management and experimental design

Tagetes patula x erecta 'Zenith Red F1' (Floranova Ltd., Foxley, United Kingdom) was used as a P-sensitive model plant. Seeds were sown in weakly fertilized peat (70 mg N, 40 mg P, and 75 mg K L^{-1}), which was adjusted with lime to a pH of 5.5. After precultivation for 10 days, seedlings were pricked individually into plastic pots (diameter 10 cm, volume 400 mL; Teku, Poeppelmann Kunststoff-Technik GmbH & Co. KG, Lohne, Germany). For each treatment, the number of planted pots was 32. The pots were split into four repeats and arranged in a randomized block design in the greenhouse. The greenhouse's climate control system was adjusted to 22/20°C (day/night) for heating and 25°C for ventilation. Plants were fertilized weekly as described in Section I. Between the fertilization events, irrigation was performed from above with deionized water to maintain adequate moisture in the growing medium according to good horticultural practices. To prevent nutrient leaching, the pots were placed into saucers. If leaching occurred, leachates were poured back into the pots. In addition, saucers were flushed twice with deionized water during cultivation and the rinse water was applied to pots to maintain the nutrients. Due to infestations of thrips and leaf miners, the plant protection agent Vertimec (Syngenta, Basel, Switzerland) was used three times at a concentration of 0.01%. After four weeks of cultivation, 90% of the plants reached flowering (marketable stage) and were harvested.

Data collection

For data collection at harvest time, pots of each treatment were pooled per replicate. First, the fresh weight of the above-ground shoots was determined. The plant material was then dried in a forced-air oven at 70°C until a constant weight was achieved, and the dry weight was subsequently recorded. For analyses of P content, the plant material was ground to a particle size <0.5 mm using a centrifugal mill (ZM1, Retsch, Haan, Germany) and digested in a mixture of HNO_3/H_2O_2 under pressure in a microwave oven (Multiwave ECO, Anton Paar, Graz, Austria) according to Miller (1998). Subsequently, P analyses were performed using ICP–OES (iCap 6000 DV, Thermo Fisher Scientific, Dreieich, Germany). The P uptake of plants was calculated by multiplying the P content by the dry weight, and the relative P use efficiency (rPUE) was expressed as the percentage of applied P.

In addition to the plant analyses, the amounts of CAL-soluble phosphate (P_{CAL}) and CAT-soluble phosphate (P_{CAT}) in the growing medium were analyzed at the start of the trial and at harvest time according to VDLUFA methods A 6.2.1.1 (Kießling and Hofmann, 2016) and 13.1.1 (Alt and Hofmann, 2004). The P in the filtrate was determined analogously to the plant analysis by ICP–OES.

The estimated plant-available P (P_{mod}) in the growing media was calculated according to Equation (2) using 0.3 for the coefficient $K_{CAL\text{-}CAT}$ in Equation (1) according to the prediction model of section I.

Equation 2:

$P_{mod} = P_{CAT} + (P_{CAL}\text{-}P_{CAT}) \times 0.3$

P_{CAT} = CAT-extractable amounts of P in the growing medium in mg pot^{-1}

P_{CAL} = CAL-extractable amounts of P in the growing medium in mg pot^{-1}

Data analysis

Minitab V18 (Minitab Inc., State College PA, USA) was used for the statistical analysis, and MS Excel (2016) was used for data visualization. For plant fresh weight as well as P content and P uptake of the plants, a two-way ANOVA using the GLM function was performed, followed by two separate Dunnett tests ($p < 0.05$) using MCP and RockP as controls. After removing the control treatments, the effects of SSA type and growing media pH on rPUE were tested by computing a two-way ANOVA, followed by Tukey tests ($p < 0.05$). The P uptake in relation to the extractable (P_{CAT}, P_{CAL}, respectively) or estimated plant-available P in the growing medium (P_{mod}) at trial start was visualized in a scatter plot. In addition, the correlation between plant P uptake and P_{CAT}, P_{CAL}, and P_{mod}, respectively, was evaluated using regression analysis.

Results

Efficacy of secondary source-P at pH 4.5

At a pH of 4.5 in the growing medium, the fresh weight of plants fertilized with secondary P sources ranged from 3.1 to 32.1 g per plant (Figure 4a). No significant differences were found between $SSA_{Trollins1}$, BC-SDG400, and STR-AIRPREX and the control treatments of MCP (28.2 g $plant^{-1}$) and RockP (28.1 g $plant^{-1}$), respectively. In contrast, the secondary P sources of DG1, BC-650, and MEPHREC-SS differed significantly from the control treatments. DG1 had a significantly higher fresh weight (32.1 g $plant^{-1}$), while MEPHREC-SS and BC-650 showed a strong reduction in fresh weight (3.1 and 4.8 g $plant^{-1}$, respectively) compared to the controls. Regarding P uptake, differences were observed between the controls and multiple secondary P sources (Figure 4b). None of the secondary P source-treatments led to a plant P uptake similar to the MCP treatment (17.4 mg pot^{-1}, equivalent to 70% rPUE). In contrast, plant P uptake obtained from RockP (12.6 mg pot^{-1}, equivalent to 50% rPUE) was achieved by BC-SDG400, and exceeded by DG1 and STR-AIRPREX (15.5 mg pot^{-1}, equivalent to 62% rPUE, and 14.0 mg pot^{-1}, equivalent to 56% rPUE, respectively). Secondary sources-P from $SSA_{Trollins1}$, BC-650, and MEPHREC-SS exhibited a lower P uptake compared to the RockP-P. Hereby, plant P uptake of $SSA_{Trollins1}$ was only slighter lower (10.9 mg pot^{-1}, equivalent to 44% rPUE), while BC-650 and MEPHREC-SS treatments showed less than 10% of the RockP treatment. Since the results for dry weight and P content corresponded highly to those of fresh weight and P uptake ($R^2 < 0.93$), they were not further considered.

Efficacy of secondary source-P at pH 6.0

At pH 6.0 in the growing medium, secondary source-P led to fresh weights ranging from 8.1 to 29.1 g per plant (Figure 4c). The resulting plant fresh weight of three secondary P sources treatments (DG1, BC-SDG400, STR-AIRPREX) was comparable to that of MCP (28.2 g $plant^{-1}$), whereas $SSA_{Trollins1}$ reached only 74% and BC-650 and MEPHREC-SS less than 10% of the MCP value. No secondary P sources exhibited fresh weight values comparable to those of the RockP control (12.3 g $plant^{-1}$). The fertilization with secondary source-P did not lead to a comparable level of plant P uptake obtained from MCP-P (16.1 mg pot^{-1}, equivalent to 64% rPUE) or RockP-P (2.4 mg pot^{-1}, equivalent to 9% rPUE), respectively. While plant P uptake derived from MCP was higher compared to that from secondary P sources, only two secondary P sources treatments (BC-650, MEPHREC-SS) resulted in lower plant P uptake compared to RockP. Analogously to efficacy at 4.5, dry weight and P content provided no additional information and are therefore not displayed.

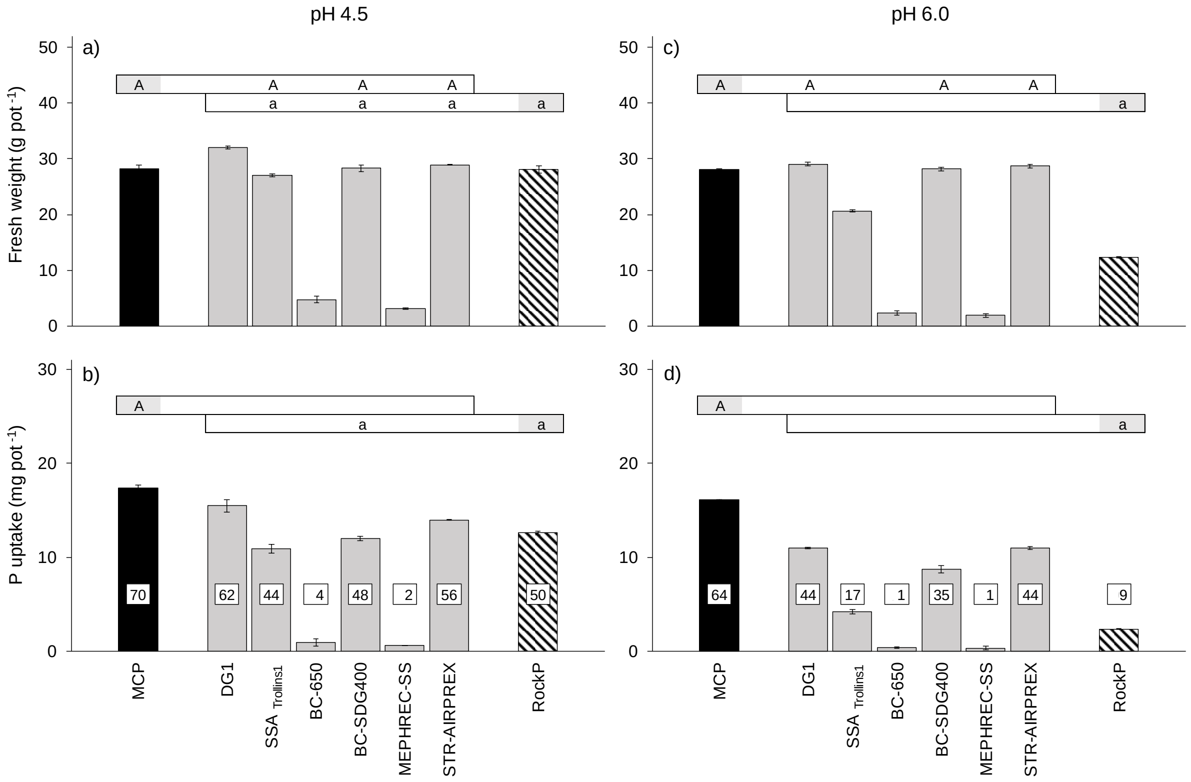

Figure 4: Fresh weight (a,c), and P uptake (b,d) of marigold plants fertilized with different secondary P sources (DG1, $SSA_{Trollins1}$, BC-650, BC-SDG400, MEPHREC-SS, STR-AIRPREX), monocalcium phosphate (MCP) or rock phosphate (RockP) after cultivation for four weeks under contrasting pH conditions (4.5, 6.0). Values in the columns of panels b and d indicate the P use efficiency in % of applied P. Secondary P sources with capital “A” did not differ significantly from the MCP control, nor did those with lowercase “a” from the RockP control (Dunnett test, $p < 0.05$). Error bars represent the standard error of the mean (n = 4).

Effect of pH on rPUE

The pH level in the growing medium significantly affected the rPUE (Figure 5). For all secondary P sources, rPUE was higher under acidic condition in the growing medium. However, the absolute difference in rPUE between pH 4.5 and 6.0 varied among the secondary P sources (Figure 6) and ranged from 1 to 27 percentage points. The largest difference in rPUE between the contrasting pH values was observed for $SSA_{Trollins1}$, which was approximately 30 times higher than for BC-650 and MEPHREC-SS, the latter sources having the lowest values. The difference in rPUE for DG1, BC-SDG400, and STR-AIRPREX, ranged from 12 to 18 percentage points, an intermediate position among the observed values.

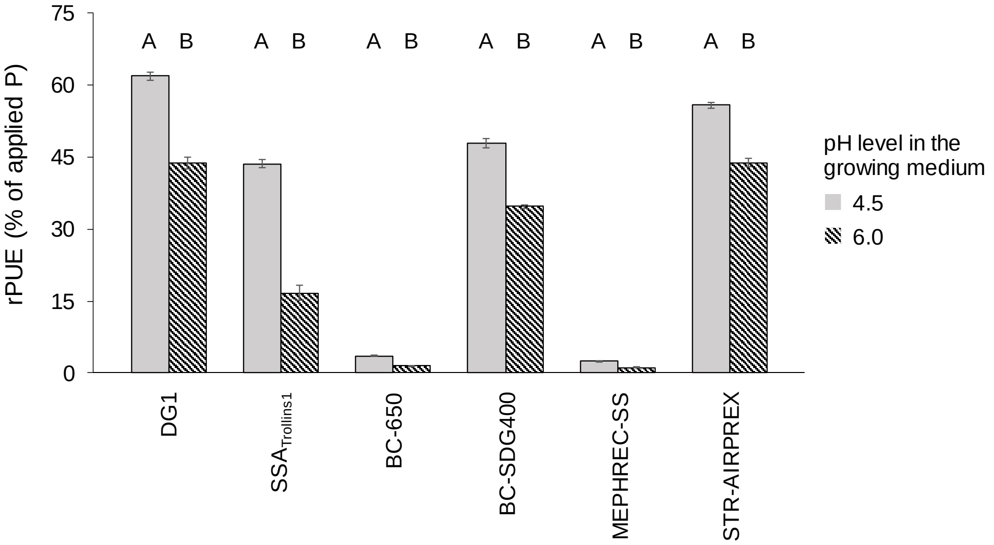

Figure 5: Relative phosphorus use efficiency (rPUE) at two contrasting pH levels in the growing medium for secondary P sources (DG1, $SSA_{Trollins1}$, BC-650, BC-SDG400, MEPHREC-SS, STR-AIRPREX) (Tukey, $p < 0.05$). Error bars indicate the standard error of mean (n = 4).

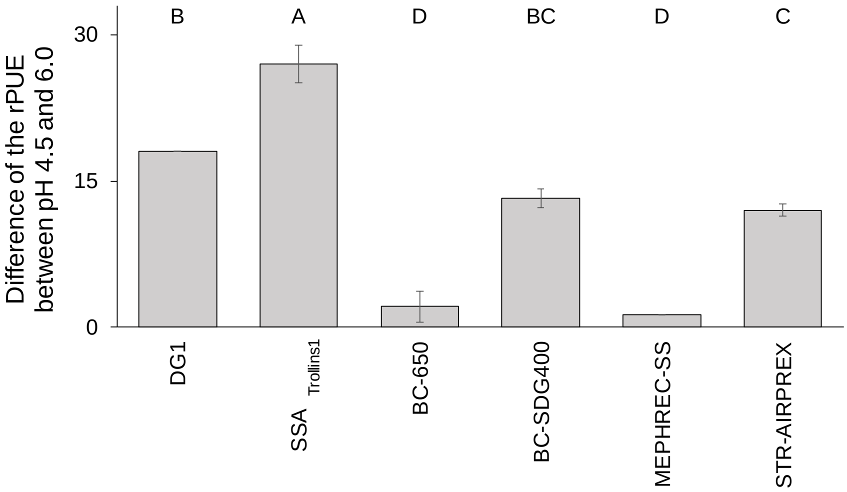

Figure 6: Difference of relative phosphorus use efficiency (rPUE) in percentage points between pH 4.5 and 6.0 for secondary P sources (DG1, $SSA_{Trollins1}$, BC-650, BC-SDG400, MEPHREC-SS, STR-AIRPREX). Different letters indicates differences between the secondary P sources (Tukey test, $p > 0.05$) Error bars indicate the standard error of mean (n = 4).

Growing media analyses

Table 3 shows that P_{CAL} was higher than P_{CAT} in almost all cases, especially at pH 6.0. For the secondary P sources at the beginning of the trial, only DG1 achieved P_{CAT} values ≥60% of applied P, whereas the remaining ranged from 2 to 58% at pH 4.5 and 1 to 35% at pH 6.0. However, DG1 did not reach the level of P_{CAT} from the water-soluble control fertilizer MCP (≥80% of applied P). In contrast to P_{CAT}, in P_{CAL}, STR-AIRPREX along with DG1 exhibited values ≥60% of applied P, while the rest of the secondary P sources ranged from 2 to 50% applied P at pH 4.5, and 3 to 42% of applied P at pH 6.0. However, STR-AIRPREX`s P_{CAL} surpassed DG1 and was on a similarly high level as MCP.

It must be mentioned that values for P_{CAT} and P_{CAL} of RockP and BC-650 at pH 4.5 must be handled with caution, since greater P_{CAT} than P_{CAL} values appear implausible due to CAL being the stronger extractant and should extract more P, as was the case at: (i) trial start at pH 6.0, (ii) at trials end, and (iii) in other observations. Hence, an interchange of CAT and CAL-labeling may have occurred during laboratory analyses.

Table 3: CAT and CAL extractable amount of phosphorus (P_{CAT}, P_{CAL}) in the growing medium (mg pot $^{-1}$) at contrasting pH (4.5, 6.0) at the start and end of the trial, after fertilization with secondary P sources (DG1, SSA$_{Trollins1}$, BC-650, BC-SDG400, MEPHREC-SS, STR-AIRPREX), water-soluble monocalcium phosphate (MCP), and rock phosphate (RockP). Values at the end of the experiment are presented as means of the biological repeats (n = 4) ± standard deviation.

Treatments		**Trial Start**		**Trial End**	
pH in the Growing Medium	**Fertilizers**	**P_{CAT}**	**P_{CAL}**	**P_{CAT}**	**P_{CAL}**
4.5	MCP	25.0	24.9	3.0 ±1.3	4.0 ±1.2
	RockP	9.0	7.0	1.3 ±0.3	1.8 ±0.5
	DG1	18.0	18.9	1.4 ±0.2	2.8 ±0.6
	SSA$_{Trollins1}$	3.1	4.0	0.7 ±0.2	2.0 ±0.0
	BC-650	1.5	0.6	0.9 ±0.1	1.0 ±0.0
	BC-SDG400	9.9	12.6	1.1 ±0.2	2.0 ±0.0
	MEPHREC-SS	0.5	0.8	0.0 ±0.0	1.0 ±0.0
	STR-AIRPREX	14.4	22.3	5.0 ±0.7	7.3 ±1.3
6.0	MCP	20.0	22.4	1.8 ±0.1	4.0 ±0.8
	RockP	1.1	3.2	0.2 ±0.3	3.5 ±0.6
	DG1	15.0	18.9	2.4 ±0.2	6.0 ±0.8
	SSA$_{Trollins1}$	0.9	2.3	0.0 ±0.0	2.0 ±0.0
	BC-650	0.3	0.8	0.0 ±0.0	1.0 ±0.0
	BC-SDG400	6.3	10.5	0.7 ±0.1	3.0 ±0.0
	MEPHREC-SS	0.3	0.6	0.0 ±0.0	1.0 ±0.8
	STR-AIRPREX	8.7	22.7	3.5 ±0.5	9.5 ±1.3

A strong correlation was found between plant P uptake and both P_{CAT} (R^2 = 0.81) and P_{CAL} (R^2 = 0.76), after four weeks of cultivation (Figure 7). However, both standard growing media extractions strongly underestimated plant P uptake in plants cultivated at pH 4.5 and after application of $SSA_{Trollins1}$. In contrast to P_{CAT}, P_{CAL} also strongly overestimated plant P uptake for the secondary P sources DG1 and STR-AIRPREX.

Numerically the best fit for plant P uptake was observed for P_{mod} (R^2 = 0.83). However, the numerical correlation difference between plant P uptake and P_{mod} and P_{CAT}, is exceedingly small.

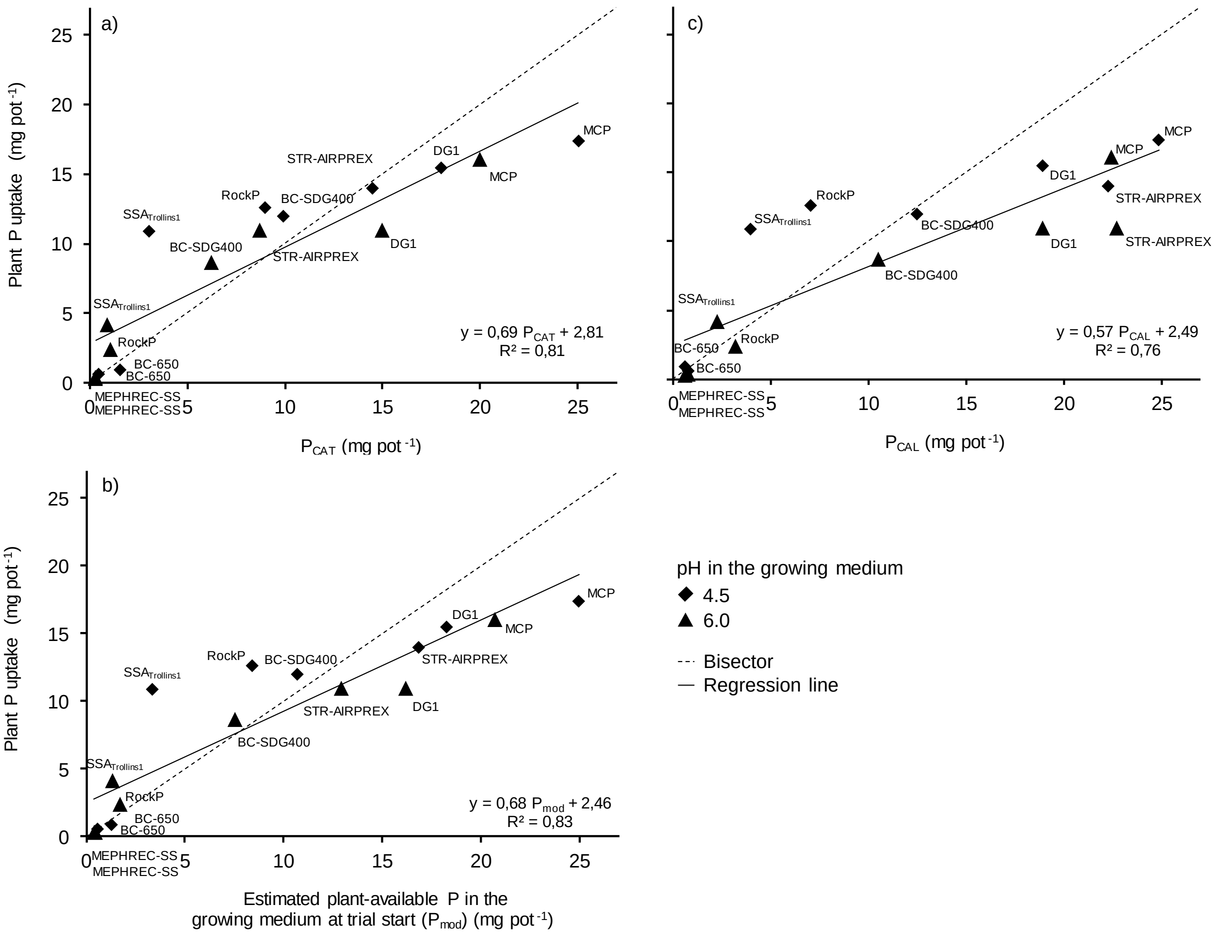

Figure 7: Relationship of phosphorus (P) uptake of marigold plants four weeks after fertilization with different secondary P sources (DG1, $SSA_{Trollins1}$, BC-650, BC-SDG400, MEPHREC-SS, STR-AIRPREX) and cultivation in growing media of contrasting pH (4.5, 6.0) to P_{CAT} (a) and P_{CAL} (c) and the estimated plant-available P (P_{mod}) (b) in the growing medium.

Discussion

Plant P availability of secondary P sources

Among the tested secondary P sources, a wide range was observed in plant growth (7–103% of the MCP control) and P uptake (2–68% of the MCP control) at growing media pH of typically 6.0 (Figure 4). While for BC-650, MEPHREC-SS, and $SSA_{Trollins1}$ a reduction in fresh weight compared to the MCP control was observed, fertilization with DG1, BC-SDG400, and STR-AIRPREX led to a similar fresh weight accumulation. In contrast, for plant P uptake no secondary source led to a level similar to MCP. These findings - except for STR-AIRPREX - fully align with previous results (section I, section II: pH trial 1) that have been previously discussed in detail. In contrast to actual findings, the struvite STR-AIRPREX exhibits a plant P uptake comparable to MCP control at the pH level 5.5–6.0 (pH trial 1). Since in pH trial 1 growing media preparation and pot filling were performed according to good horticultural practice by volume, which is less accurate than weight-based methods, it could be assumed that in contrast to the MCP treatment: (i) slightly more P was applied to the growing media blend or (ii) a higher amount of growing medium was filled into the pots for STR-AIRPREX treatment. Consequently, P supply for plants of STR-AIRPREX treatment might been slightly higher than the target 25 mg P per pot, thus causing a P uptake similar to MCP. This assumption is reinforced by a higher amount of extractable STR-AIRPREX-P in the growing medium observed in the pH trial 1, compared to the other pot trials. Compared to at a growing medium pH of 6.0, at pH 4.5, the plant performance derived from secondary source-P was higher, ranging for fresh weight from 11–114% compared to the MCP, and for plant P uptake from 3–89% compared to MCP. However, the observed plant P availability for BC-650 and MEPHREC-SS remains unusable for horticultural plant production in peat-based growing media since the observed plant parameters reached at best 17% of the values exhibited by the water-soluble reference fertilizer. However, in contrast to the other secondary P sources, BC-650 and MEPHREC-SS were of coarser structure (partly >2 mm). As known for other P fertilizers with limited solubility, grinding to a powdery form might increase the plant P availability. For the other secondary P sources (BC-SDG400, $SSA_{Trollins1}$, STR-AIRPREX, DG1), plant P availability was quite high, since plant fresh weight was comparable to (BC-SDG400, $SSA_{Trollins1}$, STR-AIRPREX) or higher than (DG1) the water-soluble MCP, and the level of plant P uptake was at least 62% of the control value. According to the data, the higher fresh weight of plants grown with DG1 compared to MCP is not linked to P availability, since P uptake was lower for DG1 than for MCP. However, as it is known that digests contain multiple nutrients in plant-available form (Möller and Müller, 2012). In the case for plants fertilized with DG1, other nutrients might have been growth promoting, even if nutrient supply was adjusted to the level of plant demand and nutrients were given in a slight surplus during the cultivation. For products exhibiting lower plant fresh weight at growing medium pH of 6.0 than MCP, $SSA_{Trollins1}$ was the only secondary P source that could reach the fresh weight level of MCP at pH 4.5. A higher plant P availability of sewage sludge ashes was also reported by Nanzer et al. (2014) for mineral soil-based plant production. However, as reported by this author, the magnitude of this effect strongly differed among ashes and was linked to the P-bearing phase, especially to the proportion of the contained CaP and Al-/Fe-P. For ashes obtained from biological sludge treatment, CaP are assumed to be more abundant than Al-/FeP, and thus ashes profit the most from acidic pH due to higher solubility of CaPs under acidic conditions. However, in addition, plant availability of Al-/FeP might be promoted by chelating effects of humic and fulvic acids preserved from peat, (Lobartini et al., 1998; Lohr et al., 2023). In contrast to the findings of pH trial 1, here $SSA_{Trollins1}$ plant P uptake was significantly lower compared to RockP control. These contradicting results may be attributed to a finer grinding of the RockP granules, which results in a slightly better dissolution of RockP-P compared to the current study. However the observed difference is very small and thus is of minor practical relevance for plant production on peat-based growing media.

Plant P availability for all secondary P sources was higher at a growing media pH of 4.5 compared to 6.0 (Figure 5). However, this effect varied between the secondary P sources (Figure 6). The increase in rPUE at pH 4.5 for BC-650 and MEPHREC-SS was negligible (<2 percentage points), but of practical relevance for the remaining secondary P sources (13–27 percentage points). For the secondary P sources derived from biogas residues (DG1, BC-SDC400) a similar intermediate level in increase in rPUE (13–18 percentage points) was observed, which could be attributed to the presence of CaP of higher crystallinity which is known to be abundant in organic residues such as biogas digests or composts (Möller and Müller, 2012, Frossard, 2002). For the struvite (STR-AIRPREX), an intermediate position of a similar level (12 percentage points) was observed. However, this result that the pH of the growing media notable effects plant P availability of struvite somehow contradicts the result obtained from the previous trial, and the knowledge gained for soil-based plant production

(Kratz et al., 2019). As outlined by Muys et al. (2021) struvites´ chemical and physical properties vary between different production procedures. Various authors (Wollmann et al., 2018, Kern et al., 2008) assume that the struvite obtained from Berliner Wasserbetriebe GmbH (STR-AIRPREX) not only contains magnesium ammonium phosphate, but also remarkably amounts of less plant-available, highly crystalline CaPs. The reason for the CaP abundance might be a less controlled precipitation process for this compared to other struvite productions. This assumption is further supported by a lower plant P availability of STR-AIRPREX compared to other struvites (Wollmann et al., 2018; Hauck et al., 2021). In this light, it seems plausible that STR-AIRPREX exhibits a better rPUE under pH 4.5 compared to pH 6.0 in the growing medium. Considering the non-sensitive behavior of STR-AIRPREX in the previous trial (pH trial 1), this might in this case be due to a higher application level of STR-AIXPREX, which makes the amount of plant available P a less limiting factor for the plant uptake. The highest difference in rPUE between growing medium pH 4.5 and 6.0 (27 percentage points) was observed for the tested sewage sludge ash ($SSA_{Trollins1}$). As already discussed, the significant increase in plant available SSA-P can be attributed to multiple factors, including acidic-soluble P compounds and chelating agents in the growing medium. Due to the relatively high plant P availability under acidic conditions in the growing medium, the increasing availability of SSA material derived from the increasing number of incineration facilities and stricter regulation for usage of SSA in soil-based plant production may promote SSA as a suitable substitute for primary P sources in soilless cultivation for crops requiring low pH (e.g., *Azalea* spp.) in the growing medium. However, since the pH’s effect on P availability differs among SSAs (Nanzer, 2012; Steckenmesser et al., 2017; Lemming et al., 2020), a comparative study with SSA of different origins is needed to derive a general conclusion regarding SSA-P’s plant availability and whether this is a suitable P-source for soilless cultivation under acidic conditions.

Prediction of plant P uptake by growing media analyses

Plants absorb P from the soil solution. Hence, plant P uptake predictions based on growing media analyses must reflect P concentration in the soil solution. Since sorption and desorption processes for P are negligible in peat (Khandan-Mirkohi and Schenk, 2009), the P concentration in the soil solution is mainly determined by the chemical equilibrium constant of the P species being fertilized. However, the chemical equilibrium constants differs among P species and are highly influenced by soil or growing media pH (Scheffer/Schachtschabel, 2018).

As shown in Figure 7, plant P uptake highly correlates with the calcium chloride + diethylenetriaminepentaacetate (P_{CAT}), and calcium-acetate-lactate (P_{CAL}) extractable amount of P in the growing media at trial start (P_{CAT}: $R^2 = 0.81$, P_{CAL}: $R^2 = 0.76$). However none of the solvents were able to reflect the promoted plant availability of $SSA_{Trollins1}$ at pH 4.5 in the growing medium. This could be attributed to CATs' and CALs' inability to reflect the promoted plant availability of Fe-/AlPs by the increased chelating effect of humic and fulvo acids in peat under acidic conditions (Lohr et al., 2023). In contrast, for the rest of the secondary P sources, a strong differentiation was visible between pH levels in the growing media, which fitted quite well to the plant P uptake. Conversely, differentiation between pH levels in the growing medium was less pronounced for P_{CAL}. This was especially true for DG1 and STR-AIRPREX where a negligible difference in between the extractable amount of P in growing medium of different pH was observed. In addition, plant P uptake was strongly overestimated in these treatments. In this light, these observations are in line with those published for products containing CaPs of higher crystallinity (Alt and Peters, 1992). As outlined in the literature, the overestimation of CaPs' plant availability by CAL is attributed to the extraction pH of 4.1, which is ensured by a strong buffering. At this low pH, CaPs' solubility is higher compared the solubility in the growing media at a pH above 4.1 (Alt et al., 1994). However, the observed differentiation between pH levels in P_{CAL} for the highly crystalline dominated RockP, somehow contradicts the reported disadvantage for CAL. It might therefore be possible that the fertilized growing medium contained too many basic components (lime, basic constituents in RockP), exhausting the buffer capacity of CAL, therefore extracting at the actual pH of the growing media like CAT does. However, in the light of the wide extraction ratio for the CAL-method of 1 + 20 (M + V) this seems to be questionable.

To overcome solvent specific limitations for hardly soluble secondary source P, the new approach by combining CAT- and CAL-extractable P amount in the growing media (P_{mod}) was assumed to be a suitable approach for predicting plant-available P in growing media. Since P_{mod} correlates strongly with P_{CAT} ($R^2 = 0.99$), P_{mod} reflects the pH driven P availability of secondary sources quite well, but did not significantly improve prediction of plant P uptake. In addition, the solvents specific limitations of not reflecting the promoted plant availability of FeP/AlP, indicates that other solvents might be needed to satisfactorily characterize plant-available secondary source-P in growing media. In addition, it has to be noted that for some products, remarkably amounts of P were extractable at trial end, which indicates that not all plant available P was taken up by the plants. This should be mentioned in future general assessments of P_{mod}.

SSA comparison trial

Hauck, D., Lohr, D., Meinken, E. and Schmidhalter, U. (2022). Phosphorus availability from German sewage sludge ashes to plants cultivated in soilless growing media of contrasting pH. *Agronomy*, 12, 2610.

Authors contribution:

Daniel Hauck: Conceptualization, methodology, investigation, formal analysis, visualization, and writing - original draft preparation.

Dieter Lohr: Supervising laboratory analyses, and writing - review and editing.

Elke Meinken: Writing - review and editing, project administration, and funding acquisition.

Urs Schmidhalter: Review and editing, and supervision.

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Article

Phosphorus Availability from German Sewage Sludge Ashes to Plants Cultivated in Soilless Growing Media of Contrasting pH

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Abstract: Sewage sludge ash (SSA) as a secondary phosphorus (P) source may help to conserve global rock phosphate deposits if used in the base fertilization of soilless growing media. Plant availability of SSA-P was studied in a pot experiment with marigolds in a peat-based growing medium of contrasting pH (4.5, 6.0). Six SSAs were included in the study and compared to water-soluble monocalcium phosphate (MCP) and rock phosphate (RockP). In addition to the efficacy of SSA-P, calcium chloride + diethylenetriaminepentaacetate (CAT) and calcium-acetate-lactate (CAL), as commonly used extractants in Germany to analyze plant-available P in growing media, were tested in terms of their ability to predict plant P uptake. No SSA reached the relative P use efficiency (rPUE) observed for MCP. However, at a growing medium pH of 4.5, the average rPUE for SSA was 70% of the MCP rPUE. Compared to RockP, at a growing medium pH of 6.0, SSAs resulted in an rPUE of nearly the same low level. In contrast, at pH 4.5, the rPUE from SSAs was mostly lower than that from RockP, and there were differences in rPUE among SSA origins. Therefore, in addition to a variation in particle size distribution, there might be differences in the P-bearing phase. Sewage sludge ashes represent a promising substitute for primary P sources only in crops requiring a low pH in the growing medium. The extractants CAT and CAL, on their own or in combination, did not reflect plant P uptake from SSA. To improve the prediction of plant-available SSA-P, solvent modifications or additional extractants might be promising and should be subjected to further research.

Keywords: fertilization; horticulture; phosphorus recycling; monoincineration ash; pH effect; secondary P source; plant production

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1. Introduction

Phosphorus (P) fertilizers are crucial for ensuring crop production [1]. However, rock phosphate (RockP) deposits primarily used for fertilizer production will be depleted within the next centuries [2,3]. Closing the P cycle in agriculture is necessary to secure sustainable use of the limited resource RockP [4–7]. In this light, P recovered from secondary sources may help close the cycle. A high potential for P recovery is found in sewage sludge ash (SSA) [8,9], which occurs in large quantities. In Germany, approximately 1.8 million tons of dry sewage sludge (SS) arise annually [10]. Nearly 70% of this sludge is incinerated with increasing occurrence [10] due to stricter regulations for the application of SS [11]. When used as fertilizer, SSA has fewer harmful environmental effects (no organic pollutants and pathogens, less volatile heavy metals) than SS [8]. In addition, the availability of SSA-P must also be considered in crop production.

In monoincinerated SSAs, the relevant P compounds driving plant P availability are different forms of iron and aluminum phosphates (FeP, AlP) as well as calcium phosphates (CaP) of higher crystallinity [12]. In soil-based crop production, Ca-associated P forms (e.g., whitlockite and hydroxylapatite) have been reported to be more available to plants than AlP and FeP (e.g., variscite and vivianite). This was especially found in acidic soils [13,14]. In SSAs, the proportion of these P forms varies among ashes [15]. This variability is due to the chemical composition of the initial sewage sludge [16] driven by the P elimination strategy of the wastewater treatment plant (P elimination with or without Al/Fe flocculants) [17] and seasonal variations in the treated wastewater [18]. Kratz et al. [15] summarized the plant availability of SSA-P from low to medium, reporting equivalents from 0 to 52% of fully plant-available P forms (e.g., monocalcium phosphate).

Besides soil-based production, relevant cropping systems use soilless growing media. In 2021, approximately 12 million cubic meters of growing media were produced in Germany [19], consisting primarily of peat and organic and mineral peat substitutes (e.g., wood fiber, green compost and clay). Base growing media fertilization utilizing SSA-P could help to conserve finite RockP reserves. However, the results concerning the efficacy of SSA-P derived from soil-based production might not be transferable to soilless cultivation, as P dynamics, mainly driven by P buffering capacity, differ between mineral soils and growing media. As the primary growing medium constituent, peat has a neglible ability to buffer P [20]. As such, the resulting higher P mobility in growing media enables roots to expand their depletion zone by approximately ten times compared to mineral soil [20]. Consequently, roots' enhanced and overlapping depletion zones promote higher spatial P accessibility in soilless cultivation. In addition, peat's low P buffering capacity also means that the chemical availability of P entirely depends on the equilibrium position between dissolved and solid P. The pH in the growing medium, among other things influenced by the cultivated crop [21], contributes to the equilibrium position depending on present P compounds. The plant availability of Ca-associated P decreases with increasing pH, whereas the reverse is true for Fe- and Al-associated P.

To the best of the authors' knowledge, the suitability of P recovered from wastewater for crop production in growing media has been investigated in only a few studies [22,23], and none of them compared different SSAs. Therefore, this was investigated in the present research work. In addition to the lack of knowledge about the efficacy of SSA-P in growing media-based crop production, the feasibility of commonly used methods of growing media analyses predicting plant available P remains unknown. To assess plant-available P in growing media, extraction-based methods established in Germany use calcium chloride + diethylenetriaminepentaacetate (CAT) and calcium–acetate–lactate (CAL) as solvents. According to Alt et al. [24], readily soluble P is well indicated by the CAT method, whereas less soluble but plant-available P reserves, such as iron and aluminum phosphates, are underestimated [25]. In contrast, CAL frequently overestimates plant P availability, especially when sparingly soluble CaP is applied or growing media are rich in clay and high in pH, respectively [24,26]. To overcome these solvent-specific limitations in over- and underestimating P pools, Hauck et al. [23] developed a new approach combining CAT- and CAL-extractable P by using secondary P sources. However, the developed model is valid for a growing medium pH of 6.0 commonly used in soilless production. Thus, it remains questionable whether this new approach is suitable to characterize the plant availability of SSA-P irrespective of the growing medium pH.

To address the identified knowledge gaps regarding plant availability of SSA-P in soilless plant production and its predictability, a pot trial was conducted using marigold (*Tagetes patula* × *erecta*) as a P-sensitive model plant. Different SSAs were tested in a peat-based growing medium under contrasting pH values (4.5 and 6.0), and their P efficacy was compared to water-soluble monocalcium phosphate (MCP) and RockP as controls. The prediction model, according to Hauck et al. [23], was used to assess P availability. We hypothesized that (1) the plant availability of SSA-P cannot compete with that of water-soluble P, (2) one single solvent is not suitable for assessing the plant availability of SSA-P through growing media analyses, and (3) the combined approach by Hauck et al. [23] improves the prediction of plant P availability, irrespective of the growing medium pH.

2. Materials and Methods

2.1. SSAs and Control Fertilizers

Six SSAs obtained from German monoi-ncineration plants (one batch each from three origins and three batches from one origin) were tested as P fertilizers in this study (Table 1). To characterize the SSAs, the particle size distribution was measured in triplicate using an SDC–Microtrac S3500 laser diffraction system (Microtrac, Montgomery Ville, PA, USA) (Table 2). In addition, after acid digestion in aqua regia [27], the total content of P and heavy metals of the SSAs was measured in duplicate with ICP-OES (iCap 6000 DV, Thermo Fisher Scientific, Dreieich, Germany) using the following wavelengths (in nm): P 213.6, As 189.0, Cd 228.8, Tl 190.8, Hg 184.9, Ni 231.6, Pb 220.3.

Table 1. Overview of the tested sewage sludge ashes.

SSA	**Incineration Facility**	**Information about the Wastewater Treatment Plant ***		
		Origin of Sewage Sludge	**Type of Wastewater**	**P Removal**
Trollins (batches 1–3)	Steinhaeule by Neu-Ulm city	Wastewater association Klaerwerk Steinhaeule	Municipal, few industrial	Al + Fe salts
Ostrau	Emter GmbH by Altenstadt city	Various bavarian wastewater treatment plants	Municipal	No data available
Luenen	Innovatherm GmbH by Luenen city	Wastewater associations, industrial companies (pharmaceutical, chemical, metal processing)	Municipal, industrial	No data available
Grosslappen	Gut Grosslappen by Munich city	Wastewater treatment plant Gut Grosslappen	Municipal, few industrial	Biological + Al salts

* Source: personal communication.

Table 2. Particle size distribution of the SSAs expressed as a percentage of the total number of particles. The total content of P is indicated in g (kg dry matter (DM))$^{-1}$ and heavy metals in mg (kg DM)$^{-1}$ of the SSAs.

SSA	**<160 µm**	**160–630 µm**	**>630 µm**	**P_{total}**	**As**	**Cd**	**Tl**	**Hg**	**Ni**	**Pb**
	% of Total Particles			**g (kg DM)$^{-1}$**	**mg (kg DM)$^{-1}$**					
Trollins1	64	36	0	67.0	14.6	1.3	<0.5 *	<0.5 *	56.1	64.2
Trollins2	51	49	0	58.5	13.8	10.5	<0.5 *	<0.5 *	49.3	65.6
Trollins3	55	45	0	59.9	13.7	11.3	<0.5 *	<0.5 *	53.3	64.9
Ostrau	34	39	27	88.6	8.0	17.4	<0.5 *	<0.5 *	39.5	45.3
Luenen	69	31	0	22.4	17.2	20.7	<0.5 *	<0.5 *	285.3 †	222.1 †
Grosslappen	65	35	0	96.4	16.6	10.4	<0.5 *	<0.5 *	39.0	103.0

* Values smaller than the declaration threshold according to the German fertilizer ordinance (2012, last amended 2019). † Values above the limit according to the German fertilizer ordinance (2012, last amended 2019).

As control fertilizers, water-soluble MCP ($Ca(H_2PO_4)_2 \cdot H_2O$, analytical grade, Sigma–Aldrich Chemie GmbH, Taufkirchen, Germany) and finely ground RockP (Hyperphos, producer unknown) were used.

2.2. Growing Medium

White peat (Patzer Erden GmbH, Sinntal-Altengronau, Germany) (Table 3) was used as the growing medium. A P-free multi-nutrient fertilizer (19-0-15) with trace elements (custom blend, Planta Düngemittel GmbH, Regenstauf, Germany) was dissolved for base fertilization in deionized water and evenly mixed into the peat at a level of 200 mg N L^{-1}. After base fertilization, the peat was split into two equal parts and limed to pH 4.5 (typical for acidophilic plants, such as Azalea) and 6.0 (typical for most ornamental plants) using Otterbein Naturkalk (85% $CaCO_3$, Zement- und Kalkwerke Otterbein GmbH und Co.

KG, Großenlueder-Mues, Germany). Subsequently, SSAs and control fertilizers were homogeneously mixed into individual growing medium portions at 70 mg aqua regia extractable P L^{-1} (equivalent to 25 mg P pot^{-1}). SSAs and RockP were applied in solid form, whereas fully water-soluble MCP was provided as a solution. To ensure equal amounts of P per pot, the growing medium was added to the pots by weight immediately before transplanting the precultivated marigold seedlings.

Table 3. Characterization of white peat. The degree of degradation according to the von Post scale and the particle size in millimeters taken from the manufacturer's declaration. The pH is indicated in $CaCl_2$ [28]; water-soluble salts are expressed in grams of KCl per liter [29], and CAT-soluble N, P and K are expressed in milligrams per liter [30].

	Degree of Degradation *	Particle Sizemm	pH ($CaCl_2$)	Salts (H_2O)g KCl L^{-1}	N (CAT)	P (CAT) mg L^{-1}	K (CAT)
White peat	H3–H5	<8	3.1	0.10	17	0	8

* From H1 (non-decomposed bog plants) to H10 (fully decomposed bog plants).

2.3. Cultivation Management and Experimental Design

Tagetes patula × *erecta* 'Zenith Red F1' (Floranova Ltd., Foxley, UK) was used as a P-sensitive model plant. Seeds were sown in weakly fertilized peat (70 mg N, 40 mg P and 75 mg K L^{-1}) limed to pH 5.5. After pre-cultivation for 10 days, seedlings were pricked individually into plastic pots (diameter 10 cm, volume 400 mL; Teku, Pöppelmann Kunststoff-Technik GmbH & Co. KG, Lohne, Germany). For each treatment, the number of planted pots was 48. They were split into four repeats and arranged in a randomized block design in the greenhouse. The greenhouse's climate control system was adjusted to 22/20 °C (day/night) for heating and 25 °C for ventilation. Plants were fertilized weekly according to the nutrient demand determined in previous trials (data not shown). For this fertilization, the P-free fertilizer used for base fertilization was dissolved in deionized water and applied in doses of 20 mg N per plant (once in week 2, twice in week 3 and three times in week 4). Between the fertilization events, irrigation was performed from above with deionized water to maintain adequate moisture in the growing medium according to good horticultural practice. To prevent nutrient leaching, the pots were placed into saucers and flushed twice with deionized water during cultivation. Leachates and rinse water were poured back into the pots. Due to infestations of thrips and leaf miners, the plant protection agent Conserve (Corteva Agriscience Germany GmbH, Munich, Germany) was used three times at a concentration of 0.075%. After four weeks of cultivation, 90% of the plants reached flowering (marketable stage) and were harvested.

2.4. Data Collection

For data collection at harvest time, pots of each treatment were pooled per replicate. First, the fresh weight of the shoots was determined. Then, the plant material was dried in a forced-air oven at 70 °C, and the dry weight was recorded after reaching weight constancy. For analyses of P content, the plant material was ground to a particle size <0.5 mm using a centrifugal mill (ZM1, Retsch, Haan, Germany) and digested in a mixture of HNO_3/H_2O_2 under pressure in a microwave oven (Multiwave ECO, Anton Paar, Graz, Austria) according to Miller [31]. Subsequently, P analyses were performed using ICP-OES (iCap 6000 DV, Thermo Fisher Scientific, Dreieich, Germany). The P uptake of plants was calculated by multiplying the P content by the dry weight, and the relative phosphorus use efficiency (rPUE) was expressed as the percentage of applied P.

In addition to the plant analyses, the amounts of CAL-soluble phosphate (P_{CAL}) and CAT-soluble phosphate (P_{CAT}) in the growing medium were analyzed at the start of the trial and at harvest time. For P_{CAL}, the extraction ratio was 1 + 20 (M + V) and the extraction time 90 min [32]. For P_{CAT}, the extraction ratio was 1 + 8 (M + V), and the extraction time 60 min [30]. After filtration, the P concentration in the filtrates were determined analogously to the plant analysis by ICP-OES.

For quality assurance of analytical data, sample duplicates were performed and reference materials were used. In cases of unexplainable differences between sample duplicates, the analyses were repeated. The use of analytical instruments was according to the manufacturers' user manual.

2.5. Statistical Analysis

Minitab V18 (Minitab Inc., State College, PA, USA) was used for the statistical analysis, and MS Excel 2016 (Microsoft Corporation, Redmond, WA, USA) was used for data visualization. For plant fresh weight as well as P content and P uptake of the plants, at first, a two-way ANOVA using the GLM function was performed. Due to the interaction between the factors SSA and pH, SSAs were compared to the controls MCP and RockP separately for each pH using Dunnett tests ($p < 0.05$). After removing the control treatments, the effects of SSA type and growing medium pH on rPUE were tested similarly using Tukey tests ($p < 0.05$ and $p < 0.001$). The P uptake in relation to the extractable P amount in the growing medium at the trial start (P_{CAT}, P_{CAL}, respectively) was visualized in a scatter plot. The same was done for the plant-available P estimated by the prediction model of Hauck et al. [23]. A correlation coefficient was not calculated due to pH-specific clusters, leading to spurious correlations and thus misinterpretations [33].

3. Results

3.1. Efficacy of SSA-P at pH 4.5

At a pH of 4.5 in the growing medium, the fresh weight of plants fertilized with different SSA types ranged from 28.8 to 30.3 g per plant (Figure 1a). No significant differences were found between the SSAs and the RockP control. Only the SSA Luenen led to a slightly higher plant fresh weight than the water-soluble MCP control. Considering the P content of the plants (Figure 1b), several significant differences were observed between the controls and the SSAs. However, in the comparison to RockP (3.8 mg (g DM)$^{-1}$), only the SSA Ostrau resulted in a lower plant P content (2.6 mg (g DM)$^{-1}$). Furthermore, three SSAs (Trollins2, Trollins3, Luenen) did not reach the level of the MCP control (4.3 mg (g DM)$^{-1}$). The most significant differences were found for plant P uptake and rPUE (Figure 1c) compared to the two controls. None of the SSAs exhibit values (P uptake: 8.6–11.6 mg plant^{-1}, rPUE: 35–46%) comparable to the MCP control (P uptake: 13.9 mg plant^{-1}, rPUE: 56%). Only for the SSA Grosslappen, P uptake and rPUE did not differ from those of the RockP control (P uptake: 12.7 mg plant^{-1}, rPUE: 51%).

3.2. Efficacy of SSA-P at pH 6.0

At a pH of 6.0 in the growing medium, all SSAs led to a significantly higher plant fresh weight (19.4–22.5 g plant^{-1}) than the RockP control (18.2 g plant^{-1}) (Figure 1d). However, none of the SSAs reached the level of the MCP control. Similar to the plant fresh weight, the P content of all SSA fertilized plants (1.4–1.5 mg (g DM)$^{-1}$) was significantly lower compared to the MCP control (4.0 mg (g DM)$^{-1}$), whereas there were no differences compared to the RockP control (Figure 1e). The most negative impact of the SSAs was observed for plant P uptake and rPUE (Figure 1f). The levels (P uptake: 3.0–3.7 mg plant^{-1}, rPUE: 12–15%) were approximately four times lower than the MCP control. Nevertheless, except for the SSA Grosslappen, plant P uptake and rPUE slightly exceeded the values of the RockP control.

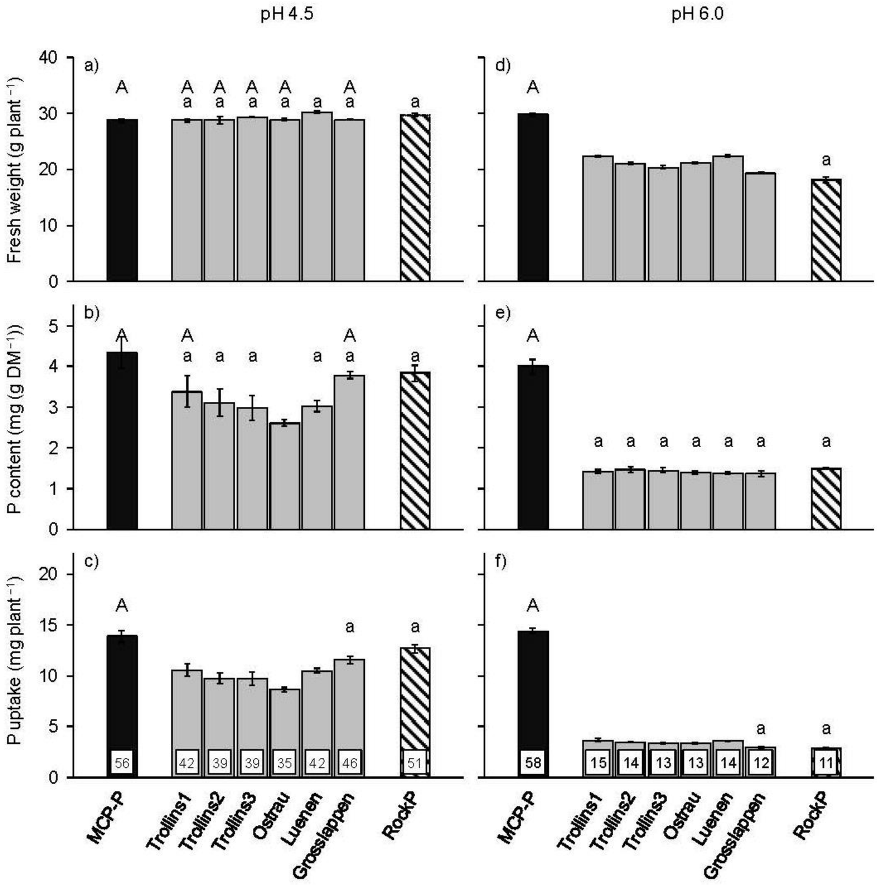

Figure 1. Fresh weight (**a**,**d**), phosphorus (P) content (**b**,**e**) and P uptake (**c**,**f**) of marigold plants fertilized with different sewage sludge ashes (Trollins1, Trollins2, Trollins3, Ostrau, Luenen, Grosslappen), monocalcium phosphate (MCP) or rock phosphate (RockP) after cultivation for four weeks under contrasting pH conditions (4.5, 6.0). Values in the columns of subfigures c and f indicate the P use efficiency in % of applied P. Sewage sludge ashes with capital "A" did not differ significantly from MCP control, nor did those with lowercase "a" from RockP control (Dunnett test, $p < 0.05$). Error bars represent the standard error of mean (n = 4).

3.3. Effect of pH on rPUE

For all tested SSAs, the pH in the growing medium significantly effected the rPUE (Figure 2). While rPUE ranged from 11.9–14.4% at the pH of 6.0, it increased up to 35–46% at a pH of 4.5. However, the extent of this pH effect depends on the SSA type (Figure 3). The rPUE difference between pH 4.5 and 6.0 was significantly lower for the SSAs Trollins2 (25 percentage points), Trollins3 (25 percentage points) and Ostrau (21 percentage points) compared to the SSA Grosslappen (35 percentage points). The SSAs Trollins1 and Luenen showed an intermediate position and did not significantly differ from the SSA Grosslappen.

3.4. Effect of SSA Type on rPUE

The rPUE of the three SSA batches originating from Trollins did not differ significantly, irrespective of the pH in the growing medium (Figure 4). In contrast, variations in rPUE were found in respect of the SSA origin. At a pH of 4.5 in the growing medium, the rPUE of the SSA Ostrau (35%) was significantly lower compared to the SSA Grosslappen

(46%). The rPUE of the SSA batches originating from Trollins and the rPUE of the SSA Luenen were at a medium level. At a pH of 6.0 in the growing medium, fertilization with the SSA Grosslappen led to a significantly lower rPUE (11.9%) than the SSAs Trollins1 (14.4%), Trollins2 (13.9%) and Luenen (14.4%), whereby the latter three did not differ among themselves. An intermediate position was observed for the rPUE of the SSAs Ostrau (13.3%) and Trollins3 (13.3%).

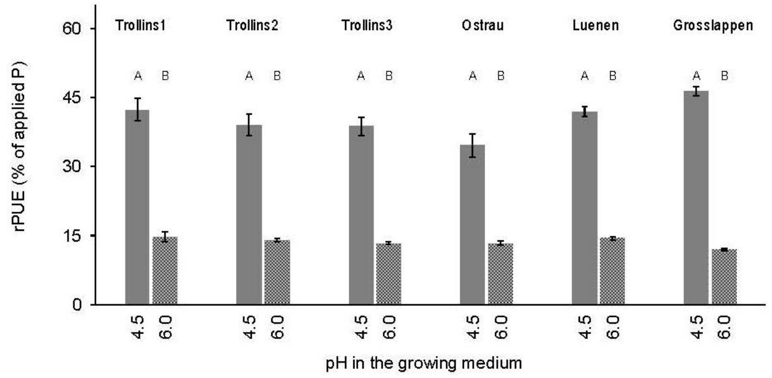

Figure 2. Relative phosphorus use efficiency (rPUE) at two contrasting pH levels in the growing medium for each sewage sludge ash (SSA). Different letters indicate differences between the pH levels for each SSA (Tukey, $p < 0.001$), and error bars indicate the standard error of mean (n = 4).

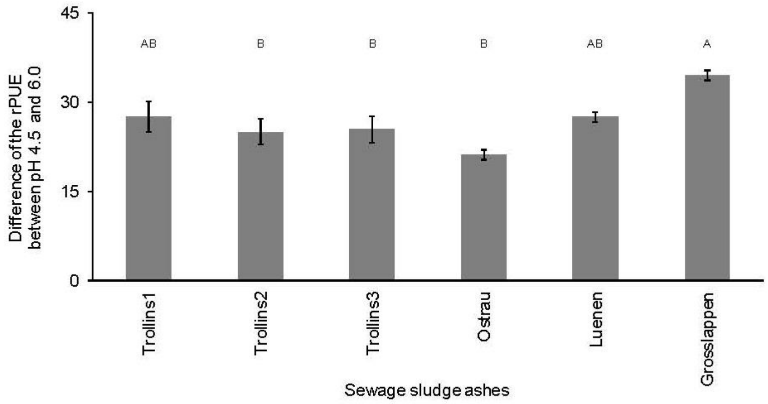

Figure 3. Difference of relative phosphorus use efficiency (rPUE) in percentage points between pH 4.5 and 6.0 for each sewage sludge ash (SSA). Different letters indicate differences between the SSAs (Tukey test, $p < 0.05$), and error bars indicate standard error of mean (n = 4).

3.5. Growing Media Analyses and Estimated Plant P Availability

Analyses of the growing media (Table 4) showed that P_{CAL} was consistently higher than P_{CAT}, whereby the difference was more evident at the higher growing medium pH of 6.0. At the beginning of the experiment, all SSAs except Luenen resulted in extremely low values ranging for P_{CAL} and P_{CAT}, ranging from 6 to 20% and 0 to 14% of applied P, respectively. For the SSA Luenen, P_{CAL} and P_{CAT} were much higher compared to the other SSAs and partly exceeded the value of the RockP control. However, the level of MCP was not reached by far. At the end of the study, only small differences in P_{CAT} and P_{CAL} were found between the SSAs.

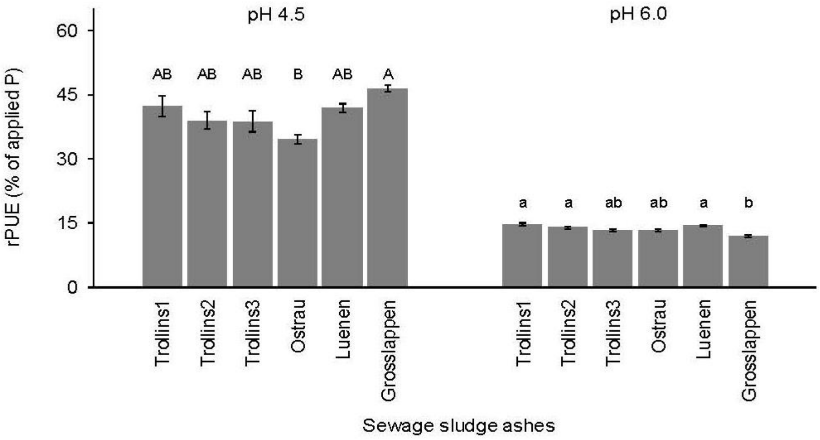

Figure 4. Relative phosphorus use efficiency (rPUE) of different types of sewage sludge ashes (SSA) at two contrasting pH levels in the growing medium. Different capital letters indicate differences (Tukey, $p < 0.05$) between the SSAs at pH 4.5, and lowercase letters indicate differences between the SSA at pH 6.0. Error bars represent the standard error of mean (n = 4).

Table 4. CAT and CAL extractable amount of phosphorus (P_{CAT}, P_{CAL}) in the growing media (mg pot^{-1}) of contrasting pH (4.5, 6.0) at the start and end of the trial, fertilized with sewage sludge ashes (Trollins1, Trollins2, Trollins3, Ostrau, Luenen, Grosslappen), water-soluble monocalcium phosphate (MCP), and rock phosphate (RockP), respectively. Details of the sewage sludge ashes are summarized in Tables 1 and 2. Values at the end of the experiment are presented as the mean ± standard deviation (n = 4).

Treatments		**Trial Start**		**Trial End**			
pH in Growing Medium	**SSA**	P_{CAT}	P_{CAL}	P_{CAT}		P_{CAL}	
4.5	Trollins1	3.1	3.6	1.4	±0.1	2.5	±0.2
	Trollins2	3.5	4.9	1.6	±0.2	2.6	±0.2
	Trollins3	1.0	3.0	1.6	±0.3	2.6	±0.4
	Ostrau	2.8	5.0	1.9	±0.3	2.3	±0.4
	Luenen	6.3	11.3	2.1	±0.2	3.0	±0.2
	Grosslappen	1.1	2.0	1.3	±0.1	2.4	±0.3
	MCP	23.9	28.9	3.1	±0.6	4.7	±0.7
	RockP	7.2	7.5	2.9	±0.2	2.6	±0.2
6.0	Trollins1	0.6	4.1	0.3	±0.1	1.4	±0.2
	Trollins2	0.8	4.9	0.6	±0.1	2.2	±0.1
	Trollins3	0.0	3.0	0.3	±0.1	1.7	±0.3
	Ostrau	0.6	4.9	0.7	±0.2	2.1	±0.1
	Luenen	2.7	12.7	1.5	±0.2	6.2	±0.6
	Grosslappen	0.2	1.4	0.2	±0.2	1.0	±0.1
	MCP	18.4	25.7	2.9	±1.3	4.7	±0.7
	RockP	0.3	5.5	0.7	±0.4	2.6	±0.2

As shown in Figure 5, neither P_{CAT} nor P_{CAL} could predict plant P uptake. While P_{CAT} generally underestimated P uptake (5 to 74%), the relationship between P uptake and P_{CAL} was less clear. If the SSA Luenen is disregarded, P_{CAL} reflected plant P uptake quite well at a growing medium pH of 6.0. However, there was an underestimation at the lower pH of 4.5, similar to with P_{CAT}.

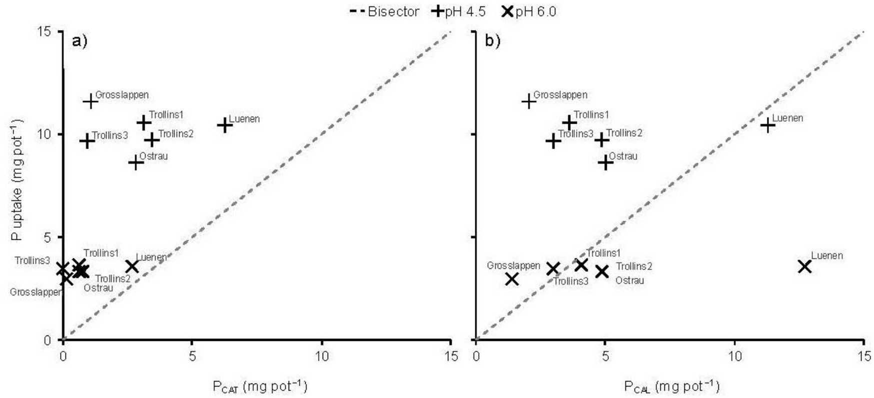

Figure 5. Relationship of phosphorus (P) uptake of marigold plants four weeks after fertilization with different sewage sludge ashes (Trollins1, Trollins2, Trollins3, Ostrau, Luenen, Grosslappen) and cultivation in growing media of contrasting pH to P_{CAT} (**a**) and P_{CAL} (**b**) at the trial start in the growing medium.

The amount of plant available P estimated by the prediction model of Hauck et al. [23] combining P_{CAT} and P_{CAL} also did not match the P uptake of plants (Figure 6). At a growing medium pH of 4.5, an underestimation of more than 50% was observed for most of the SSAs. At pH 6.0, the underestimation was less serious, but there was also an overestimation for the SSA Luenen.

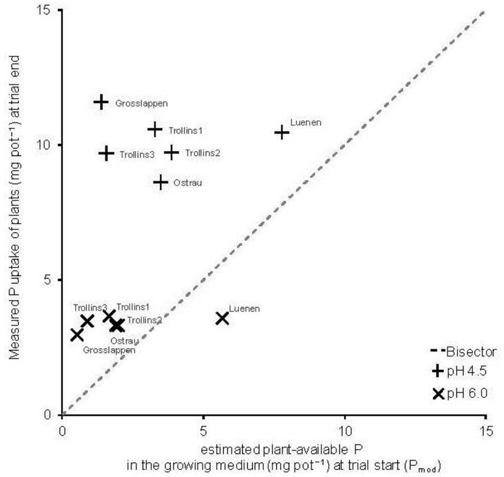

Figure 6. Relationship of the measured phosphorus (P) uptake of marigold plants four weeks after fertilization with different sewage sludge ashes (Trollins1, Trollins2, Trollins3, Ostrau, Luenen, Grosslappen) and cultivation in growing media of contrasting pH to the estimated amount of plant-available P by the model accoring to Hauck et al. [23] in the growing medium at the trial start based on P_{CAT} and P_{CAL}.

4. Discussion

4.1. Plant P Availability of Sewage Sludge Ashes

Concerning the investigated plant parameters, none of the tested sewage sludge ashes (SSAs) could compete with the water-soluble reference fertilizer monocalcium phosphate (MCP) at a growing medium pH of 6.0 (Figure 1). This was also the case for plant phosphorus (P) uptake at a growing medium pH of 4.5 (Figure 1c). Hence, our first hypothesis that plant availability of SSA-P cannot compete with that of MCP-P can be accepted.

At a growing medium pH of 6.0, which is common for most horticultural crops, plant uptake of SSA-P was only approximately one-fifth of the water-soluble MCP-P, but was slightly higher compared to rock phosphate (RockP)-P for most of the products (Trollins batches 1–3, Ostrau, Luenen) (Figure 1f). This poor plant availability of SSA-P has already been demonstrated for Trollins1 in a peat-based growing medium [23,34]. It agrees with the observations for soil-based plant production [15]. As outlined in the literature, poor P availability is mainly caused by the P-bearing phase. In addition to calcium phosphates (CaPs) of higher crystallinity (e.g., whitlockite ($Ca_3(PO_4)_2$) [35], hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) [36]), SSA might contain further P compounds such as aluminum phosphates (e.g.,variscite ($AlPO_4$) [35]), iron phosphates (e.g., strengite ($FePO_4$) [12]), and other heavy metal-associated phosphates (e.g., lead phosphate [37]) as well as magnesium phosphate (farringtonite ($Mg_3(PO_4)_2$) [36]). According to the findings of Römer [13] in sand culture, aluminum phosphates (AlP) showed, in contrast to iron phosphates (FeP), a higher plant P availability than apatite present in RockP. In this light, a certain proportion of AlP could explain the slightly higher plant availability of SSA-P compared to RockP-P. Another explanation might be that not all Ca-associated P compounds in SSA are fully transformed into apatitic structures during the combustion. In addition, magnesium phosphates are reported to be highly plant-available [13].

In contrast to a growing medium pH of 6.0, SSA-P was more plant-available in a growing medium of higher acidity (Figure 1). At pH 4.5, the plant fresh weight of the SSA treatments even reached the level of the water-soluble reference fertilizer MCP (Figure 1d). However, for plant P content (Figure 1b), only two SSA treatments (Trollins1, Grosslappen) resulted in a level comparable to the MCP treatment, and for plant P uptake (Figure 1c), no SSA treatment attained the MCP value. The higher plant availability of SSA-P under acidic conditions agrees with the results of our previous study [38] and those in soil-based plant production [39,40]. The observed increase in plant availability of SSA-P at a low pH could be attributed to a high proportion of P compounds of higher crystallinity, such as Ca- and Pb-associated phosphates, releasing plant-available P into the aqueous phase under acidic conditions [41,42]. However, the presence of AlP and FeP in the P-bearing phase of SSA is also evident at pH 4.5, as most of the SSA treatments (Trollins batches 1–3, Ostrau, Luenen) led to a lower plant P uptake and thus to a lower relative phosphorus use efficiency (rPUE) than RockP (Figure 1c). According to common knowledge, the solubility of FeP and AlP is poor under acidic conditions [15,43]. However, this result contrasts with the findings of Lohr et al. [25]. In their study, a growing medium pH of 5.5 compared to 6.5 resulted in a slight increase in plant P availability for AlP and in a high increase for FeP. The authors attribute this result to a high chelating effect of fulvic and humic acids in growing media under acidic conditions. Due to the contrasting effect of a low pH on plant availability of AlP and FeP, the role of these P compounds in SSAs used in growing media-based production systems remains unclear, and consequently, additional investigations are needed.

As indicated by the relatively uniform differences in plant P availability between SSAs and the controls, the comparison among SSAs revealed only a few significant differences in rPUE (Figure 4). At a growing medium pH of 6.0, the rPUE ranged from 11.9% to 14.7%. This small range at a low level is of minor practical relevance regarding adequate plant nutrition. In contrast, at the lower pH of 4.5, acid-soluble phosphates in SSAs resulted in a higher rPUE, varying markedly between 34.5% (Ostrau) and 46.4% (Grosslappen). The low rPUE observed for Ostrau might be linked to the particle size distribution. As revealed by laser diffraction analyses, Ostrau was the only SSA with particles >630 µm (numerically 27%, Table 2), and thus the coarsest product. Therefore, in addition to the P-bearing phase, particle size seems to be a key factor for plant P availability. This assumption is supported by previous studies [34] and the findings of other authors [44].

However, the importance of particle size distribution on plant P availability depends on the pH of the growing medium. At a low pH, the dissolution of acid-soluble P compounds is diminished by a high amount of coarse particles due to a small reaction surface [45]. This particle size and pH interaction is causative for Ostrau having the lowest rPUE difference between pH 4.5 and 6.0 of the growing medium (Figure 3). Although there is no significant difference in rPUE between Ostrau and the other SSAs, except Grosslappen, the rPUE at a growing medium pH of 4.5 was positively correlated ($R^2 = 0.77$) with the number of particles <160 µm of the SSAs. This further underlines the role of particle size in plant P availability.

4.2. Prediction of Plant P Uptake by Growing Media Analyses

To predict plant P uptake, a growing medium extractant must reflect the P concentration in the aqueous phase of the growing medium, as plants take up only dissolved P. The concentration of dissolved P in growing media made of peat depends entirely on the chemical equilibrium constant of the fertilized P compounds. The release of sorbed P into the aqueous phase is negligible due to its low P buffer capacity [20].

As shown in Figure 5, for most SSA treatments, plant P uptake did not match the P amounts in the growing medium extractable by calcium chloride + diethylenetriaminepentaacetate (P_{CAT}) and calcium-acetate-lactate (P_{CAL}). In addition, the plant P uptake differentiation did not fit both extractants. Therefore, the second hypothesis that a solvent on its own is not suitable for assessing the plant availability of SSA-P is confirmed. An underestimation of plant P uptake was generally observed for the CAT method, especially with a growing medium pH of 4.5 (Figure 5a). This underestimation might be attributed to the chelation of Fe and Al from non-CAT-soluble FeP and AlP [25] by humic acids releasing plant-available orthophosphates into the aqueous phase [46]. This effect is more pronounced with a growing medium pH of 4.5, since the chelating effect of humic acids is generally promoted under acidic conditions [47] and was shown in detail for Fe(III) by Van Dijk [48].

The positive effect of Fe and Al chelation on plant P availability might also explain the underestimation of plant P uptake by P_{CAL} with a growing medium pH of 4.5 for all SSAs except Luenen, where P_{CAL} nearly matched plant P uptake (Figure 5b). The differing behavior of Luenen might be due to a higher proportion of acid-soluble P compounds, such as CaP of higher crystallinity, compared to the other SSAs. This is supported by the overestimation of plant P uptake by P_{CAL} at the higher pH of 6.0 of the growing medium, according to Alt and Peters [49], typically for CaP of higher crystallinity. In addition to CaP, we assume that other highly acid-soluble P compounds are present in Luenen due to higher P_{CAL} values compared to RockP (Table 3), which consists of highly crystalline CaP. As such, lead phosphates (PbP) of higher crystallinity are possibly present in the SSA Luenen, which was the only industrial sewage sludge, for the following reasons: (i) PbP appears in industrial sewage sludges [37], (ii) PbP of higher crystallinity is more acid-soluble than CaP of higher crystallinity [42], and (iii) Pb ions are known to substitute Ca ions in apatites [50], which are formed during sewage sludge combustion.

The limitations of CAT and CAL show that these extractants can hardly characterize P's plant availability from secondary sources such as SSA differing in P compounds [14,15,23,51]. In this light, Hauck et al. [23] suggested improving the prediction of plant availability of P from secondary sources in growing media by combining P_{CAT} and P_{CAL} to P_{mod}: $P_{CAT} + (P_{CAL} - P_{CAT}) \times 0.3$. As shown by the comparison of Figures 5 and 6, the highest difference between P_{mod} and P_{CAT} and P_{CAL} was observed for Luenen. However, the estimation of plant-available P in the growing medium by P_{mod} was also not satisfactory since plant P uptake from Luenen was underestimated by P_{mod} at a growing medium pH of 4.5 and still overestimated at a pH of 6.0 (Figure 6). For the rest of the SSAs, P_{mod} did not improve plant P uptake prediction. At a growing medium pH of 6.0, the prediction power of P_{mod} and P_{CAL} for plant P uptake was nearly the same. The observed underestimation at a growing medium pH of 4.5 is not surprising, as P_{mod} is derived from an additive combination of P_{CAL} and P_{CAT}, which both strongly underestimate plant P uptake. This could be because P_{CAT} and P_{CAL} cannot comprehensively reflect the presumed chelation of Fe and Al from FeP and AlP.

The positive effect of chelation on plant availability of FeP and AlP could potentially be included in P_{mod} by an increased concentration of the chelator DTPA in the CAT extractant or by choosing another chelating agent (e.g., EDTA). Alternatively, an additional alkaline solvent (e.g., sodium bicarbonate) might be helpful to assess plant-available SSA-P by extracting FeP-P and AlP-P [52], which was indicated for growing media by Handreck [53].

5. Conclusions

The rPUE of SSA depends highly on the pH of the growing medium. At a commonly used pH of 6.0 in soilless plant production, the rPUE of SSAs ranged from 12 to 15% compared to 58% for the water-soluble reference fertilizer (MCP). This low level contradicts the use of SSA as base fertilizer for soilless growing media in the horticultural production of non-acidophilic crops. In contrast, at a pH of 4.5, a higher rPUE level from 35 to 46% was observed for SSAs compared to 56% for MCP. Consequently, SSA seems to be a promising substitute for primary P sources such as MCP for crops requiring low growing medium pH. However, several points must be considered before establishing SSAs in horticultural practice. An adequate quantity of SSA fertilizer cannot be generalized, since rPUE among SSAs varies at a pH of 4.5 of the growing medium. Furthermore, the required SSA quantity could not be derived by growing media analyses based on CAT and CAL, as extractable P in the growing medium did not reflect the plant uptake of SSA-P. To improve the prediction of plant-available SSA-P, solvent modifications or additional extractants might be promising and should be studied in further research. Overall, economic feasibility as another important factor for SSA establishment should be subjected to further investigation.

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4.3. Section III

Summary

In addition to the chemical characteristics, such as the P-bearing phase, the physical properties of a material, such as its grain size, are also influenced by the P recovery technologies and the subsequent processing of secondary P sources. As known for mineral soil-based plant production, hardly soluble fertilizers like RockP and SSA, plant-availability is not only driven by P-bearing phase but also by grain size and it can be enhanced by grinding. This section investigates (i) the possibility to improve plant P availability for the secondary sources by grinding, and (ii) examines if the new prediction model (P_{mod}) by Hauck et al. (2021) (section I) reflects the plant P uptake derived from fertilization of secondary P sources having different grind sizes.

Two pot trials (grain size trial 1, grain size trial 2) were conducted using secondary P sources of different grind sizes. In the grain size trial 1, plants were fertilized at a base of 30 mg P per pot using SSA_{Ostrau}, MEPHREC-SS, and STR-AIRPREX without further treatment (coarse particles), and as powder, which was obtained by short term grinding in a disc mill. As benchmark, grinds of RockP (powder, coarser granules), and MCP was used. For all three secondary P sources and RockP the fine grinds led to higher plant P uptake compared to the coarse fraction and thus grinding improved the availability. However, absolute enhancement in P uptake varied among the tested fertilizer: SSA_{OSTRAU} >> STR-AIRPREX > MEPHREC-SS > RockP. Except for the finely ground STR-AIRPREX, P uptake of plants for other secondary P sources was less than from water-soluble control MCP. However, coarse STR-AIRPREX and finely ground SSA_{Ostrau} exhibited approximately 60% of MPCs plant P uptake, whereas it was less than 5 % for the remaining treatments.

Plant P uptake and the estimated amount of plant-available P in the growing media at trial start by the new approach combining CAT- and CAL-soluble P was closely correlated (R^2 = 0.87). However, P uptake for the finely ground sewage sludge ash was strongly underestimated by the new approach, which is in line with the findings from the previous studies. Considering the slight uneven distribution of data, the finding indicates, that the new approach reflects quite well the effect of grain sizes on available secondary source-P.

Within the grain size trial 2, for secondary P sources exhibiting the worst plant P availability among the trials (BC-650, MEPHREC-SS), it was tested if very fine grinds (<0.2 mm) obtained by long term milling (several minutes) increase the plant P availability to a similar level as exhibited by MCP compared to coarser fractions obtained from short-term milling (0.3–0.5 mm, 1–2 mm). Only the finest grinds, exhibited an increase in plant P availability, while for coarser grinds the P uptake by plants was on a negligible low level. However, the level of P uptake for particle sizes <0.2 mm did not reach by far the level of the water-soluble reference fertilizer MCP. Thus, BC-650 and MEPHREC-SS, respectively seem to be not suitable as fertilizer for plant production.

Due to a lack of variation in plant P uptake derived by the coarser grinds, the data set was not suitable for a generalized conclusion whether P_{mod} can characterize the effect of grain size on plant availability for secondary source-P. However, within the finest grinds, no difference between plant P uptake and the estimated amount of plant-available P in the growing medium by P_{mod} was found for MEPHREC-SS, whereas for BC-650, P_{mod} significantly underestimated P uptake. However, since this underestimation in BC-650 was numerically very low and thus is of minor importance in respect of P_{mod}`s suitability to reflect the plant P uptake, the results support the assumption that P_{mod} is able to reflect the effect of grain size on plant availability obtained from secondary source-P.

The findings obtained from the two trials highlight the importance of grain size as driver for plant P availability, which can be improved by applying finer particle sizes. However the magnitude of this effect differs among the secondary P sources. For the tested secondary P sources, improved availability was only of practical relevance for the coarse SSA. According to the data, P_{mod} reflects quite well the effect of grain size among the different secondary P sources.

Grain size trial 1

Hauck, D., Lohr, D., Max, J., and Meinken, E. (2022). Plant availability of phosphorus in recycled fertilizers from wastewater treatment - effect of grain size. *Acta Horticulturea, 1317*, 207-214.

Authors contribution:

Daniel Hauck: Conceptualization, methodology, and writing –review and editing.
Dieter Lohr: Supervising laboratory analyses, formal analysis, visualization, and writing - original draft preparation.
Johannes Max: Supervision.
Elke Meinken: Writing - review and editing, project administration, and funding acquisition.

Plant availability of phosphorus in recycled fertilizers from wastewater treatment - effect of grain size

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Abstract

Due to the depletion of global phosphorus deposits and stricter legal regulations regarding phosphorus loads in wastewater, the recovery of phosphorus from wastewater is gaining more and more interest. There are plenty of techniques to recover phosphorus from wastewater and sewage sludge. Depending on the recovery technique and the subsequent processing, the availability of phosphorus to plants can differ widely. However, beside the chemical characteristics also grain size of the fertilizer, as is well known from rock phosphates, might be essential for plant availability. Thus, the plant availability of phosphorus in three wastewater-based fertilizers - sewage sludge ash (SSA), Mephrec and struvite - in relation to their grain size was evaluated in a pot trial with marigold. Recycled P fertilizers were applied to a peat based growing medium on basis of 30 mg P per pot (1) as received and (2) after grinding to a fine powder with a disc mill. For comparison, rock phosphate (Hyperphos) was treated in the same way and water soluble mono calcium phosphate (CaP) was used as benchmark. Marigold seedlings were pricked in 10 cm pots and cultivated for seven weeks according to common horticultural practice in a glass-sheltered greenhouse. With exception for finely ground struvite, P uptake of plants from the recycled fertilizers was significantly less than from CaP. However, P uptake from coarse struvite and powdered SSA was at least 50 % of P uptake from CaP, whereas it was less than 5 % for the remaining treatments. For all three recycled fertilizers as well as for the used rock phosphate grinding significantly increased P uptake, but only for SSA the effect was of practical relevance. The results reveal that grinding can improve the plant availability of phosphorus in recycled fertilizers, but the effect strongly depends on the chemical characteristic of the product.

Keywords: growing medium, sewage sludge ash, struvite, marigold

INTRODUCTION

Due to high variability of feedstocks as well as recovery techniques – including subsequent processing – availability of phosphorus in recycled fertilizers from wastewater treatment can differ significantly. This is even true for products using the same recovery technique. Kratz et al. (2019) reviewed the relative solubility of phosphorus from a broad range of recycled fertilizers: For 19 different precipitates they report between 37 and 100 % of total P to be soluble in citric acid. Additionally, to the difference in solubility between Ca- and Mg-precipitates (Huygens and Saveyn, 2018), the degree of crystallization, which is decisively influenced by processing conditions as initial pH, ion concentration, and temperature (Kim et al., 2004; Wang and Nancollas, 2008; Sutiyono et al., 2016), plays an important role for plant availability (Römer, 2006; Myus et al., 2021). Furthermore, for chemical treated sewage sludge ashes, the range of total P to be soluble in citric acid was 23 to 92 %. First, this might be due to the ratio of phosphorus bound to aluminum, iron and calcium, respectively, which strongly depends on the used flocculating agent (Krogstadt et al., 2005). Second, incineration temperature as well as additives (e.g. Na_2SO_4, $MgCl_2$) affect chemical solubility of phosphorus and thus availability of P to plants from these products (Steckenmesser et al., 2017; Müller-Stöver et al., 2021). However, besides the chemical structure also the physical properties – in particular grain size – are important for agronomic performance of recycled fertilizers. As outlined by various authors for rock phosphate-based fertilizers, grinding can improve solubility and plant availability of phosphorus (e.g. Sander and Eghball, 1988; Lim et al., 2003; Plotegher and Ribeiro, 2016). Müller-Stöver et al. (2021) also reported this for incineration ashes of sewage sludges. However, all of the research was done in mineral soils, in which phosphorus mobility is about ten time less than in growing media used in soilless culture (Khandan-Mirkohi and Schenk, 2008). Thus, this results cannot be simply transferred, although recent research indicate similarities for P availability from recycled fertilizers in soilless culture compared to mineral soils (Ehmann et al., 2019; Hauck et al., 2021a; Hauck et al., 2021b). In the current research, the influence of grain size on P availability was evaluated for three wastewater based recycled fertilizers in comparison to rock phosphate in peat media.

MATERIAL AND METHODS

Treatments

The three used recycled fertilizers were struvite from precipitation in a municipial wastewater treatment plant using the AirPrex® process (Kabbe et al., 2014), an ash from mono incineration of municipal sewage sludge (SSA), and Mephrec®, a slag material produced in a high-temperature melting process (Scheidig et al., 2009). The three products were firstly used as received and secondly finely ground in a disc mill (Figure 1). Additionally, a commercial, granulated rock phosphate (Hyperphos) was treated in the same way. As benchmark the control was fertilized with water soluble mono calcium phosphate (CaP), which was purchased from Sigma-Aldrich (Schnelldorf).

Figure 1. Struvite, SSA, Mephrec and Hyperphos (from left to right) as received (upper row) and after milling (lower row)

Experimental procedure

Phosphorus fertilizers were applied on basis of total phosphorus content, which was analyzed via ICP-OES after aqua regia digestion. Each plant received 30 mg P as basic fertilization, which was admixed evenly into the growing medium right before seedlings were pricked. As growing medium a baltic sod peat (H3 - H5, 0 - 8 mm, Patzer Erden, Sinntal-Jossa) was used. The pH was adjusted to 6.0 using limestone (Zement- und Kalkwerke Otterbein, Großenlüder-Müs). Basic fertilization with 200 mg N and 165 mg K per liter plus trace elements was applied by a mixture of a custom-blended P free water soluble fertilizer (14+0+19) and Ferty 10 (Planta, Regenstauf) as well as analytical grade calcium nitrate and ammonium nitrate (Bernd Kraft, Oberhausen).

Marigold seedlings (*Tagetes erecta* x *patula* 'Zenith Red F1', Weigelt Samen, Grolsheim) were pre-cultivated for about two weeks and then – in calendar week 44 – pricked into 10 cm pots with a volume of 480 ml (Teku Terra 10, Pöppelmann, Lohne). Pots were placed randomized in four replicates – with 13 plants per treatment and replicate – in a glass-sheltered greenhouse. To avoid phosphorus losses, pots were placed in saucers. To return potentially leached phosphorus back to pots, saucers were flushed at the end of the experiment and water was poured on top of the pots. In the beginning, heating and ventilation set points were 20 and 22 °C during day and night time, respectively. After four weeks temperatures were lowered by 2 °C. If solar irradiation was below 10 kLux, from two hours before sunrise until two hours after sunset, supplementary light (irradiance of about 5 kLux) with sodium high-pressure lamps was applied. Plants were fertilized – with exception of phosphorus – using the same mixture as for basic fertilization and irrigated with deionized water on demand according to good horticultural practice. Two, four and six weeks after potting, one pot per treatment and replicate was taken and pooled samples were analysed for pH, soluble salts as well as content of nitrogen, phosphorus and potassium (VDLUFA, 2016) to adjust nutrient supply.

Continuously during the experiment, plant growth was visually rated. At the end of the experiment – seven weeks after potting – the remaining ten plants were cut off and fresh weight of shoots was measured. Afterwards, plants were dried to weight constancy at 60 °C in a forced-air oven and dry weight of shoots was recorded. The dried plant material was finely ground and analysed for total P content via ICP-OES after pressure digestion with a mixture of HNO_3/H_2O_2 in a microwave oven (Miller, 1998). P uptake of plants was calculated from dry weight and P content in plant tissue. Additionally to plants samples, pooled growing media samples from the ten pots per replicate were analysed for soluble phosphorus using $CaCl_2$/DTPA (CAT) and calcium-acetate-lactate solution (CAL) according to VDLUFA (2016).

Data analysis

Fresh and dry weight of shoots as well as P content and P uptake for each treatment firstly was compared pairwise with the control receiving CaP by a one-way ANOVA combined with a Dunnett test. Afterwards, the control was excluded from the data set and a two-way ANOVA followed by a post-hoc Tukey test was calculated for further examination of the grain size effect. Furthermore, P uptake of plants was correlated to CAT as well as to CAL soluble phosphorus in the growing media at the beginning of the trial. The level of significance for ANOVA was set to 0.05. Data pre-processing and visualization was done with Microsoft Excel®2016, and Minitab V18 (Minitab Inc., State College PA/USA) was used for statistical analysis.

RESULTS AND DISCUSSION

Plant development

Already two weeks after potting first symptoms of P deficiency occurred on plants fertilized with Hyperphos or Mephrec, irrespective of grain size, as well as with coarse sewage sludge ash (Figure 2). If sewage sludge ash was applied as fine powder, plant growth was slightly reduced compared to the control with CaP, but no typical deficiency symptoms appeared. Plants receiving struvite either as coarse granulate or as fine powder, showed a comparable growth than plants fertilized with CaP.

Figure 2. Plants fertilized with CaP, struvite, SSA, Mephrec and Hyperphos (from left to right) as received (upper row) and after milling (lower row) two weeks after potting.

During the further cultivation, the differences described after two weeks became more and more obvious and the effect of grain size was particularly pronounced for sewage sludge ash (Figure 3). Whereas plants fertilized with struvite or fine powdered sewage sludge ash attained a similar size as plants fertilized with water soluble CaP, plants receiving coarse sewage sludge ash as well as Mephrec or Hyperphos - irrespective of grain size - only showed poor further growth from week two to four. However, for the fertilizers Mephrec and Hyperphos growth was increased with decreased grain size.

Figure 3. Plants fertilized with CaP, struvite, SSA, Mephrec and Hyperphos (from left to right) as received (upper row) and after milling (lower row) four weeks after potting.

Plant availability of phosphorus from recycled fertilizer

As shown in figure 4[a] plants fertilized with struvite had a comparable growth as the control plants receiving water soluble mono calcium phosphate (CaP). However, for P uptake this is only true for the finely ground struvite (Figure 4[b]). The high phosphorus availability of struvite is in line with results of Ehmann et al. (2019) from a similar trial with sunflower and marigold and also with findings from pot trials using mineral soil (Myus et al., 2021). However, Wollmann et al. (2017) reported a lower plant availability from AirPrex® struvite compared to a struvite, which was obtained from a different precipitation process. On the other hand, these authors found a similar phosphorus availability for AirPrex® struvite and Mephrec, which is somehow conflicting to the current results. However, thereby it has to be considered that Mephrec used in the current study was produced in a pilot plant and, as reviewed by Kratz et al. (2019), agronomic performance of Mephrec is highly variable depending on properties of the used sewage sludge ash and process conditions. Results for shoot dry weight and P content were comparable to those for shoot fresh weight and P uptake, and thus are not discussed further.

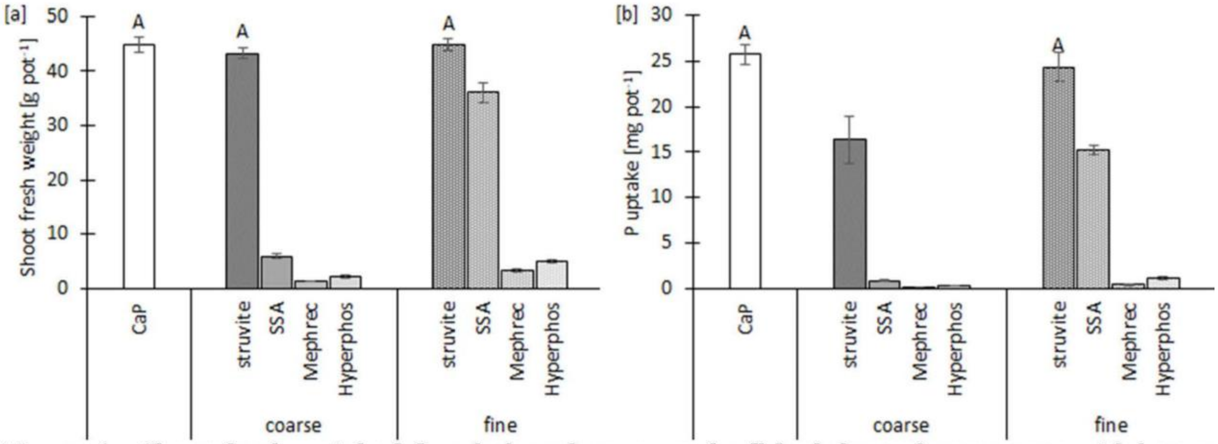

Figure 4. Shoot fresh weight [a] and phosphorus uptake [b] of plants (treatments with letter A are not significant different from treatment CaP (Dunnett test with $p \leq 0.05$), error bars indicate standard error of mean, n = 4)

Grain size effect on phosphorus availability

In a second step, the effect of grain size on P availability was viewed in detail by a two-way ANOVA without the CaP control. Thereby a significant interaction between the type of fertilizer and grain size was found. Thus, the data set was split along fertilizers and one-way ANOVAs were calculated for each subset. For Hyperphos, SSA and Mephrec a significant increase of shoot biomass and P uptake was observed for fine grounded materials (Figure 5[a]+[b]). However, for struvite this is only true for P uptake, but not for shoot fresh weight. Notwithstanding the significant interaction indicated by two-way ANOVA, a positive effect of decreasing grain size on phosphorus availability can be seen. It was most pronounced for SSA, considerably for struvite and at least significant in statistical terms for Mephrec and Hyperphos, but without practical relevance.

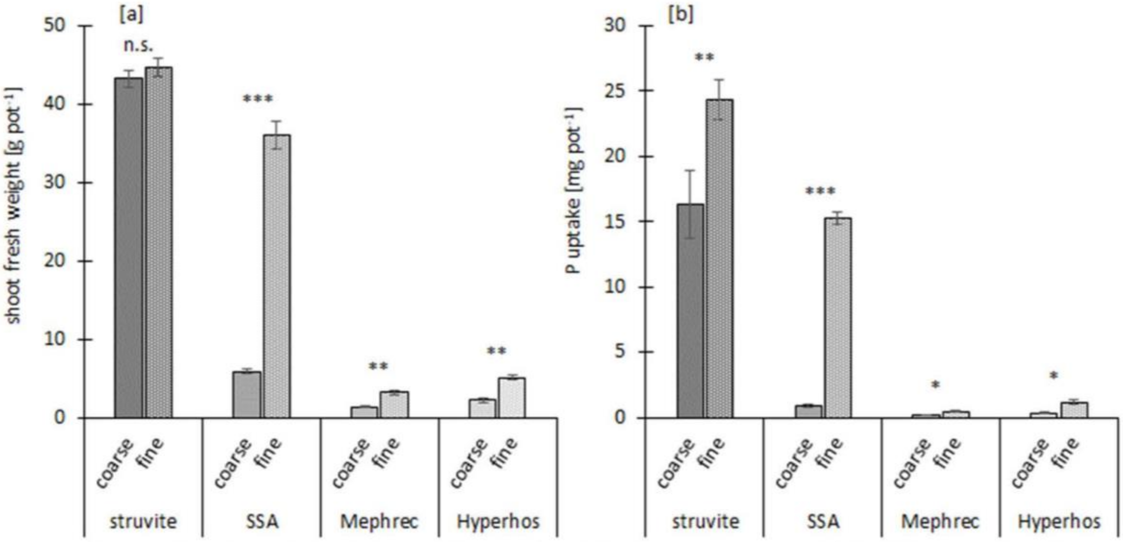

Figure 5. Shoot fresh weight [a] and P uptake [b] of plants (n.s., *, **, ***: not significant or significant different with $p < 0.05$, 0.01 and 0.001, respectively (Tukey test); error bars indicate standard error of mean, n = 4)

The differences in magnitude of grain size effect for the four fertilizers are probably related to their chemical structure. As outlined by Rajan et al. (1992), the effect of grinding on P availability of rock phosphates increases with their reactivity. Coincident results were reported for sewage sludge based recycled fertilizers by Müller-Stöver et al. (2021). This indicates that phosphorus compounds in SSA are easily plant available in principle. Lemming et al. (2020), Joseph et al. (2019) and Steckenmesser et al. (2017) elucidate the impact of P removal method – biological or chemical with iron or aluminum as flocculants – and incineration conditions on phosphorus solubility. The high plant availability of SSA used in the current research is in line with the results described by these authors as the sewage sludge originated from biological phosphorus elimination from wastewater.

The remarkable grain size effect for struvite on P uptake might explain the somehow conflicting results for P fertilizing effects discussed above. According to Myus et al. (2021), grain size distribution of struvites from different processes, but also of those from the same process, can vary significantly. For five different AirPrex® struvites the mass percentage of particles below 1 mm ranged between 68 and 98 %, which is comparable to the differences between coarse (80 %) and fine struvite (98 %) in the current research. The negligible effect of grain size for Mephrec and Hyperphos indicate a poor solubility of phosphorus compounds. The low solubility and subsequent poor plant availability of rock phosphate at higher pH values is a well-known fact (Rajan et al., 1996). In contrary, plant availability of Mephrec is highly variable (Kratz et al., 2019). According to Severin et al. (2013) and Römer and Steingrobe (2018), Mephrec has a similar chemical structure as Thomas slag (silico-carnotite; Dickens and Brown, 1971), which is rated to be readily available to plants (Stevens, 1987; Mengel, 1997; Römer, 2006). In line therewith, a quite high P availability from Mephrec –

about 60 % compared to water soluble $Ca(H_2PO_4)_2$ – is described by Wollmann et al. (2019) However, in the current research P uptake from Mephrec was even less than from Hyperphos, what is similarly reported by Zeggel et al. (2015). Perhaps even the finely ground material was still not fine enough. Heinitz et al. (2013) found a significant increase of P use efficiency if Mephrec was milled finer than 0.5 mm compared to 0.5 to 1.6 mm, whereby also in the current research > 98 % by mass was below 0.5 mm for the fine Mephrec.

Estimation of phosphorus availability from analysis of growing media

As discussed in detail by Kratz et al. (2019) the prediction of agronomic performance of recycled fertilizers is not satisfactorily solved yet. Especially due to interactions between phosphorus and physicochemical properties of the growing medium (pH, buffer capacity, P mobility), analysis of fertilizers alone is not a sound indicator for P availability. Furthermore, Hauck et al. (2021b) showed for various recycled fertilizers that neither CAT nor CAL, which are commonly used in Germany for analysis of plant available P in growing media (VDLUFA, 2016), separately reflect P uptake by plants very well. Instead, they propose a new approach combining CAT and CAL soluble P in the following way:

$$P_{up} = P_{CAT} + (P_{CAL} - P_{CAT}) \cdot 0.3$$

P_{up} = P uptake by plants [mg plant^{-1}]
P_{CAT} = CAT soluble P in the growing media at start of the trial [mg plant^{-1}]
P_{CAL} = CAL soluble P in the growing media at start of the trial [mg plant^{-1}]

As it can be seen in Figure 6, this approach is also suitable to depict effect of grain size. However, due to the uneven distribution of data points, the coefficient of determination of 0.87 has to be considered with caution. Furthermore, the P uptake from finely ground SSA is significantly underestimated. This might be due to a remarkable proportion of readily plant available aluminum phosphates, although P elimination was done biologically (Wild et al., 1996; Steckenmesser et al., 2017). These phosphorus compounds are probably not soluble in the acidic-buffered CAL (pH 4.1) solution (Penn and Camberato, 2019) and might be strongly underestimated by CAT, although extraction is done nearby the pH of the growing medium (Alt and Peters, 1992). This assumption is supported by a negative correlation between aluminum concentration and CAT soluble phosphorus reported by Balík et al. (2019).

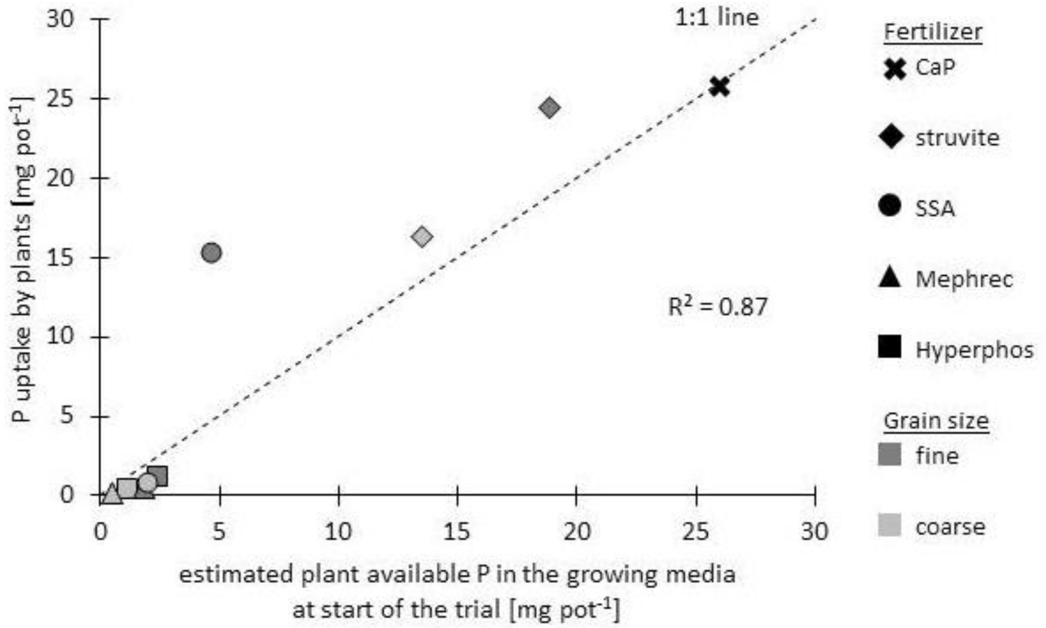

Figure 6. Relationship between estimated plant available P in growing media deduced from CAT and CAL extractable P (= $P_{CAT} + (P_{CAL} - P_{CAT}) \cdot 0.3$; Hauck et al., 2021b) at the day of potting and P uptake by plants

CONCLUSION

Indeed, grain size had a significant effect on P availability from recycled fertilizers. But only for struvite and sewage sludge ash the magnitude of the effect was of practical relevance, as phosphorus availability from Mephrec remained poor. The increase of P availability by decreased grain size is quite well reflected by a combination CAT and CAL soluble phosphorus in the growing media at the date of potting.

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Grain size trial 2

The following contains unpublished results based on a plant trial (grain size trial 2) that focused on two objectives: (i) determining the possibility of fine grinding for increasing the plant availability of the two secondary P sources, which exhibited the lowest plant P availability among the trials (BC-650, MEPHREC-SS) to a rate comparable to that of water-soluble MCP; and (ii) investigating whether the estimated plant-available P, obtained by combining CAT- and CAL-extractable P in the growing medium, is able to reflect the effect of grain size on plant P availability. Therefore, BC-650 and MEPHREC-SS were ground separately into three different particle sizes (<0.2 mm, 0.3–0.5 mm, 1–2 mm). Fractions of grain size were produced by processing individual batches with a combination of milling and subsequently sieving, till 90% of the batches' weight exhibited the aimed range of grain sizes.

Results and Discussion

Efficacy of secondary source-P at different grain sizes

After four weeks of cultivation, the plant fresh weight was on a low level for particle sizes of 0.3–0.5 and 1–2 mm for both secondary P sources (BC-650 and MEPHREC-SS), ranging from 1.8 to 2.5 g pot^{-1} (Figure 8a). In contrast to these grain sizes, the application of particle sizes <0.2 mm led to approximately 10 times higher fresh weight for BC-650 (21.5 g pot^{-1}), and 7 times higher value for MEPHREC-SS (12.1 g pot^{-1}), respectively. This findings are supported by Müller-Stöver et al. (2021), who reported an increase in fertilization efficacy for sludge-based products of lower plant availability after finely grinding. However, none of the applied grain sizes of secondary-P led to a plant fresh weight similar to that of the control MCP (38.5 g pot^{-1}). The findings in plant fresh weight were comparable to those in P uptake (Figure 8b). MCP's level of plant P uptake (16.1 mg pot^{-1}, equivalent to 64% rPUE) was by far not reached by BC-650 and MEPHREC-SS, irrespectively of the applied grain sizes. However, applying particle sizes <0.2 mm led to an approximately 10 times higher values for plant P uptake for BC-650 (3.5 mg pot^{-1}, equivalent to 14% rPUE) and MEPHREC-SS (2.1 mg pot^{-1}, equivalent to 8.3% rPUE), compared to the coarser grinds. Since dry weight and P content corresponded highly to those of fresh weight and P uptake ($r^2 > 0.99$), they were not further considered.

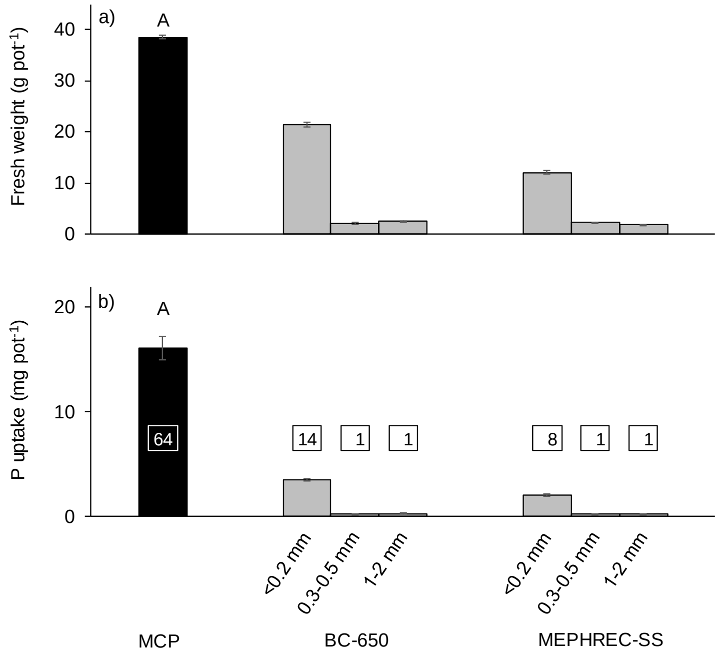

Figure 8: Fresh weight (a), and P uptake (b) of marigold plants fertilized with different secondary P sources (BC-650, MEPHREC-SS) of different grain sizes (<0.2 mm, 0.3-0.5 mm, 1-2 mm), and monocalcium phosphate (MCP) as control after cultivation for four weeks. Values in the columns of subfigures b indicate the P use efficiency in % of applied P. Secondary P sources with capital "A" did not differ from MCP control (Dunnett test, $p < 0.05$). Error bars represent the standard error of mean ($n = 4$).

Effect of grain size on rPUE

For both secondary P sources, applying particle sizes <0.2 mm strongly increased rPUE compared to particle sizes of 0.3–0.5 and 1–2 mm, which exhibited a comparable low level of rPUE (Figure 9). For BC-650, the rPUE of the finest grain size exceed the coarser ones by 14 times (14.1% rPUE), and for MEPHREC-SS by 10 times (8.3% rPUE). Similar is known for the rPUE of RockP, where P availability of the hardly soluble apatitic structures can be increased when particle sizes below 0.1 mm are applied (Lim et al., 2003).

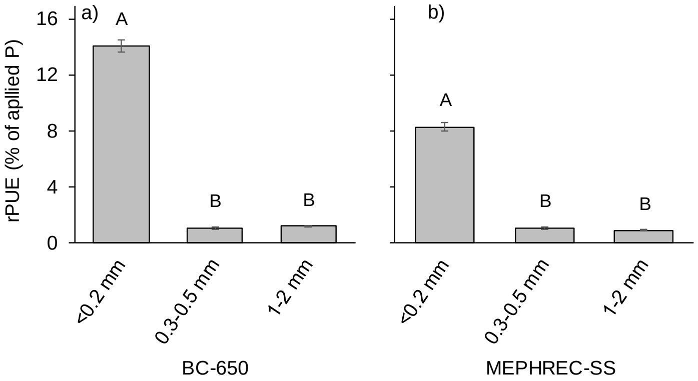

Figure 9: The relative phosphorus use efficiency (rPUE) in percentage of applied P for the secondary P sources BC-650 (a), and MEPHREC-SS (b) of different grain sizes (<0.2 mm, 0.3-0.5 mm, 1-2 mm). Different letters indicate differences between the grain sizes (Tukey test, $p < 0.05$), and error bars indicate standard error of mean ($n = 4$).

Growing media analyses

At trial start, for CAT- and CAL-extractable amounts of P of growing medium fertilized with MCP was on comparable high level (>90% of applied P). In contrast, secondary P sources of different grind sizes, exhibits values of a very low level, ranging from 0 to 7% and 3 to 26% of applied P, for P_{CAT} and P_{CAL}, respectively. Unlike P_{CAT}, P_{CAL} differentiated secondary P sources of different grain size and was negatively correlated with particle size. This differences between P_{CAL} and P_{CAT} remains noticeable at trial end.

Table 4: CAT- and CAL-extractable amount of phosphorus (P_{CAT}, P_{CAL}) in the growing medium (mg pot^{-1}) fertilized with the secondary P sources (MEPHREC-SS, BC-650) of different grain size (in mm), and water-soluble monocalcium phosphate (MCP) at the start and the end of the trial. Values at the end of the experiment represents the mean of the biological repeats (n = 4) ± standard deviation.

		Trial Start		**Trial End**	
Fertilizers	**Grain Size**	**P_{CAT}**	**P_{CAL}**	**P_{CAT}**	**P_{CAL}**
MCP		23.2	23.5	3.7 ± 0.8	6.0 ± 1.4
MEPHREC-SS	<0.2	0.2	6.4	0.2 ± 0.1	3.4 ± 0.0
	0.3-0.5	0.0	1.5	0.2 ± 0.0	1.4 ± 0.2
	1-2	0.0	0.8	0.2 ± 0.0	0.7 ± 0.1
BC-650	<0.2	0.5	2.9	1.7 ± 0.1	2.2 ± 0.1
	0.3-0.5	0.0	1.2	0.2 ± 0.0	0.7 ± 0.2
	1-2	0.0	0.9	0.2 ± 0.0	0.7 ± 0.1

Due to the lack of variation in plant P uptake among the treatments, the data set is not suitable to derive a general conclusion to the question if the commonly used growing media extraction methods are able to predict plant P uptake of secondary P sources of different grain sizes. In addition, coarser grinds of the secondary P sources only led to a negligible low amount of plant P uptake. However, ground to particle sizes <0.2 mm, fertilization with BC-650 and MEPHREC-SS, respectively led higher level of P uptake and its variation. Therefore, these values were compared to the estimation of plant-available P derived from the growing medium analyses at trial start (Figure 10). Among all values for the soluble amount of P in the growing medium only P_{mod} for MEPHREC-SS the value did not differ from the actual plant P uptake. For MEPHREC-SS, plant P uptake was underestimated by P_{CAT}, and overestimated by $P_{CAL.}$ This can be expected in the presence of higher crystalline CaPs. Since MEPHREC-SS is obtained from metallurgic processing of sewage sludge and lime, it can be assumed that such calcium phosphates of high crystallinity are formed and embedded into a highly inert vitreous phase. Those embedded CaPs became accessible due to the product`s strongly increased reaction surface as result of the finely grinding and thus are well reflected by P_{mod}, as already described in previous sections. For BC-650, the extractable amounts of P in the growing medium (P_{CAT}, P_{CAL}, or combined P_{mod}) underestimated the plant P uptake. This is in line with previous results, and properly due to the reason to CATs and CALs disadvantage to reflect Fe/AlPs (Lohr et al., 2023), which could be present in BC-650 as a residual of the wastewater P-elimination using iron and aluminum salts during the processing of sewage sludge which was used for carbonization.

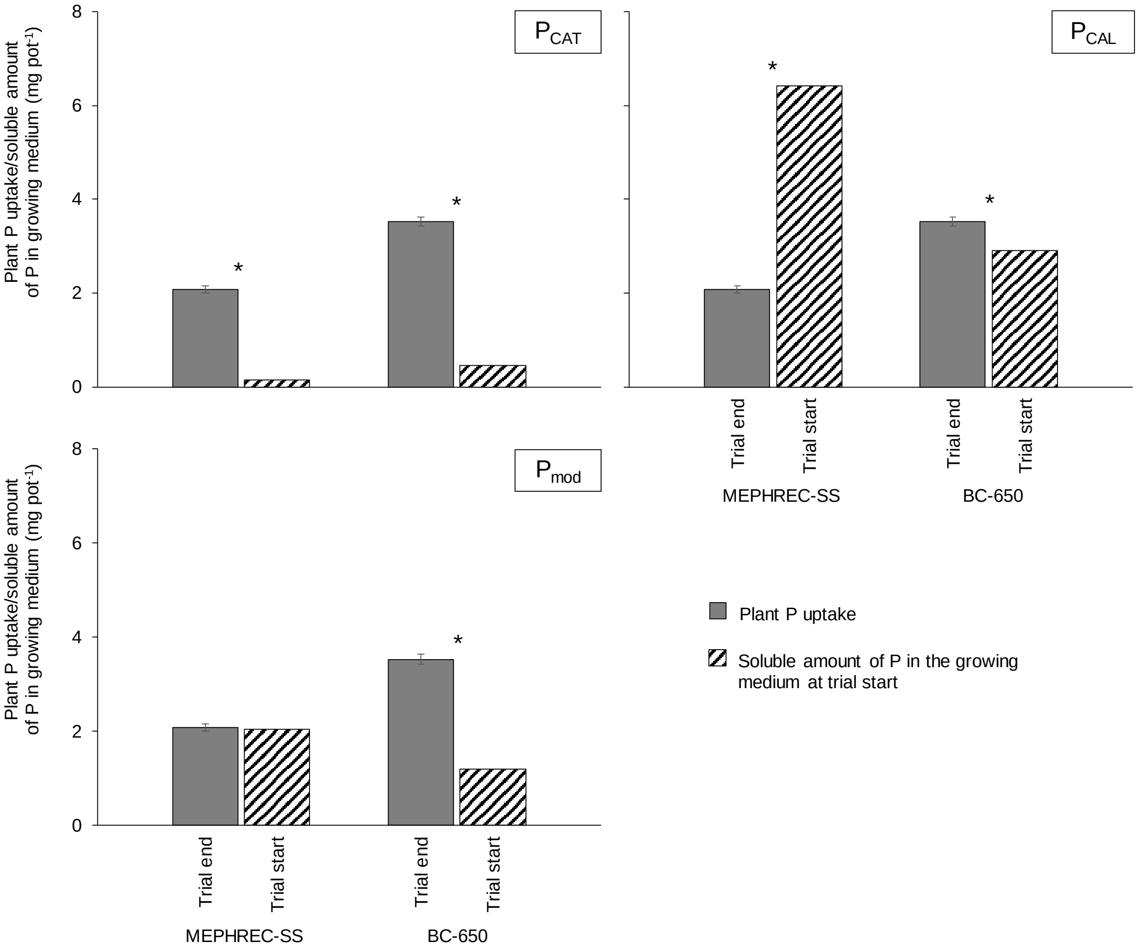

Figure 10: P uptake of plants (mg pot^{-1}) after fertilization with finely ground (<0.2 mm) secondary P sources (MEPHREC-SS, BC-650) and cultivation for four weeks and compared to the soluble P in the growing medium by P_{CAT} and P_{CAL} alone or combined (P_{mod}) at trial start (mg pot^{-1}). Error bars represents standard error of mean of the biological repeats (n = 4), asterisk indicates significant differences between plant P uptake and plant-available P in growing medium (one sample t-test, $p < 0.05$).

5. General discussion

As RockP based-fertilizers are essential for modern plant production systems, the globally sparsely distributed, depleting reserves of RockP are of strong geo-political and agro-economical relevance. To conserve these reserves, and increase independence of primary P resources, a reuse of P from waste streams (secondary sources) and a subsequently implementation of secondary source-P in crop production systems is crucial (Scholz et al., 2019). To implement secondary source-P in plant production, alongside other factors (quantitative availability, environmental security, economic viability), the plant availability of secondary P sources needs to be suitable to promote plant growth. This plant availability must also be reflected by growing media analyses, to help growers to adjust their fertilization management according to the plant needs.

5.1. Secondary P sources in growing media-based crop production

In growing media-based production of crops, P supply to plants is at the beginning provided by the growing medium itself (prefertilized-P or growing media constituent-P), and subsequently by application of a fertilizer solution (Schmilewski, 2018), which typically starts shortly after potting (a few days to weeks). Since most secondary P sources are poorly water-soluble (Kratz et al., 2019; Table 1), secondary source-P seems to be in particular suitable for base fertilization of growing media. In Germany, approximately 8.1 million cubic meters of more or less fertilized growing media are annually produced (IVG, 2023). Under the assumption of the annual production and the average level of plant-available P in growing medium (65 mg P L^{-1} (CAT-extractable): DIN, 2005), the roughly estimated demand for secondary source-P needed for base fertilization of growing media produced in Germany is in the order of 530 t plant available P $year^{-1}$. Considering this estimation, it must be noted that P levels differ widely between different growing media, and some growing media constituents themselves contain remarkably high amounts of plant-available P (e.g., compost, biogas digest). Thus, the estimated quantity of P used for growing media base fertilization is likely to be lower. Taking into account the total amount of secondary source-P contained in various waste streams - which is estimated to be approximately 380,000 t P $year^{-1}$ for Germany alone (Wiesler et al., 2020) - the potential to fully replace highly processed primary source-P used for growing media base fertilization with secondary source-P becomes clear. However, the direct transferability from the total amounts of recovered P to the amount of P that plants need to grow must be handled with caution, since plant availability differs among secondary P sources (Römer, 2006; Wollmann et al., 2018; Kratz et al., 2019; Duboc et al., 2022; section I-III). Therefore, different amounts of secondary source-P are required to maintain biomass accumulation depending on the secondary P source.

In this respect, the findings about plant availability of secondary source-P in peat-based growing media with a pH of around six (as typical for horticultural crop production) suggests, that among the 22 different secondary P sources studied here, precipitated struvite-forms (STR-AIRPREX, STR-SLURRY, STR-GALV, STR-STUTTGART) are the most promising substitutes for highly processed, water-soluble primary source-P (section I-III). Since plant growth and plant P uptake was in most cases on similar high level compared to the reference fertilizer (screening trial, pH trial 1), the amount of struvite-P needed for optimal plant growth can be considered equal to the required amount of the primary source-P. This finding is in accordance with many previous studies (Römer, 2006; Duboc et al., 2017; Kratz et al., 2019). However, it must be noted that one struvite (STR-AIRPREX) exhibited slightly less P uptake compared to the reference fertilizer, which was attributed to the product's chemical purity (presence of less plant-available CaP of higher crystallinity, Table 2) and a coarser particle size (Figure 3). A cultivation at lower pH conditions enhanced this plant availability, and grinding of the original product to a powdery structure led to a plant P availability comparable to the water-soluble reference (pH trial 2, grain size trial 1).

In contrast to the highly plant-available struvites, two secondary P sources (cinder product MEPHREC-SS, sewage sludge-based biochar BC-650) showed a negligible plant availability among the plant trials (section I-III), which was also reported previously (Zeggel et. al., 2015; Appel and Friedrich, 2017). This plant availability was improved under acidic conditions in the growing medium (section II) or by grinding the original material to a fine powder (section III). However the degree of enhancement was too low to be of practical relevance for growing media-based plant production.

For the remaining 16 secondary P sources (five untreated feedstocks, eight thermally and two thermochemically treated feedstocks, one precipitation product) the observed plant availability at growing medium pH of six was quite high when applied as powder. Here, the observed plant growth was comparable or just slightly reduced compared to the control (section I-III), whereas the average observed plant P uptake derived by secondary source-P was approximately 50% of the control value (section I-III). Consequently, it can be assumed that twice the amount of secondary source-P would be needed to obtain similar plant P uptake as a highly processed primary P source. However, since the plant P uptake among these secondary P sources varied widely between 19–90% compared to the water-soluble reference, a generalized recommendation about the amount needed for growing media-based plant production under pH conditions of approximately six should be handled with caution.

From the remaining 16 products, 8 (one untreated feedstock: biogas digest; seven thermally treated feedstocks: six sewage sludge ashes, one biochar, Table 2) were tested under acidic conditions in the growing medium (section II). Here, in contrast to the findings for growing medium pH values of around six (P uptake: 19–68% compared to the control value), at pH levels <5, the observed range of P uptake derived by secondary sources varied less (P uptake 62–89% compared to the control value). The average P uptake was approximately 75% compared to the control value. Consequently, under acidic conditions in the growing media, 1.3 times the amount of secondary source-P is needed to substitute the water-soluble P derived from the limited rock phosphate reserves. Since, (i) different forms of higher crystalline CaPs, which are known to be more available under acidic conditions (Dorozhkin, 2011), and (ii) FePs and AlP, for which plant P availability is promoted by chelating effects of humic acids especially under acidic conditions (van Dijk, 1971; Boguta et al., 2019; Yang et al., 2022) are suspected to be contained in the majority of the secondary P sources (Table 1), it is perhaps not surprising that the plant availability of these secondary P sources increased under the conditions of growing media-based production common for acidophilic plants. However, it has to be noted that 75% of the tested products were SSAs. Thus the provided findings, except for sewage sludge ashes, likely pertain more to SSA and should be considered indicative. Consequently, additional research is needed and should be focused on other secondary P sources to derive broader conclusions. Despite the relative constantly high plant P availability among different SSAs at pH <5, smaller variations were attributed to the P-bearing phase and differences in particle size distribution (section II). However, when applied as fine powder, these differences were of minor practical relevance (section II). Worth mentioning, one SSA (SSA_{Ostrau}) was received as a remarkably coarser grind which, when applied as received, significantly reduced the plant availability of this secondary P source (section III).

Conclusively, despite the lower plant P availability of most secondary P sources compared to highly processed primary P sources in plant production systems based on growing media, the total amount of secondary source-P recoverable from German waste streams is by far enough to fully substitute P derived from the limited primary P reserves in German growing media production. However, since the total amount of recovered-P is only 80% of what is needed for crop production based on mineral soils (Wiesler et al., 2020), this may lead to competition for P between crop production systems.

Although different aspects regarding the plant availability of secondary P sources and consequently their suitability to replace highly processed primary source-P used in growing media base fertilization were mentioned, there are still knowledge gaps, which future studies should address to derive more specific recommendations.

The model plant *Tagetes* ssp. was used in the investigations, since its P sensitivity was described in the literature (Khandan-Mirkohi and Schenk, 2009; Ehmann et al., 2019) and it is a typical ornamental crop produced in potted production. However, plant species can differ in their P acquisition mechanisms. Consequently, plants' efficiency to use secondary source-P might differ remarkably in growing media based-plant production. Thus different P efficacy of secondary P sources among different plant species commonly produced in pots (e.g., herbs, ornamentals, vegetables, and woody shrubs) should be investigated in future to complement the findings obtained by the current studies.

As growing medium, only white peat was used here, since mined peat as a growing medium constituent has played the most important role for potted production over the last years due to its beneficial chemical and physical properties and cheap procurement costs. However, the usage of peat as primary growing media constituent has been discussed controversially over the years, due to the massive negative environmental impacts of peat mining (Winkler and DeWitt, 1985; Kędzior et al., 2022). To address this issue, in Germany there is a governmental ambition to fully replace peat in growing media for hobby purposes by 2026 and to substitute large amounts of peat in growing media used for professional purposes by 2030 (BMEL, 2022). In this light, growing media constituents such as compost, wood fiber and clay become more relevant. However, these constituents differ remarkably in their chemical and physical properties to peat (BMEL, 2022) and thus may led to different P dynamics in the growing media. For instance, growing media primarily based on peat have a negligible P buffer capacity (Khandan-Mirkohi and Schenk, 2009), while for growing media with high portions of clay, clay's P buffer capacity plays an important role in the P dynamics (Binner, 2014). Thus, more research is needed to understand P dynamics in multicomponent growing media-secondary source-P systems.

On an economic level production costs of secondary P sources vary, at least in part due to differences in processing requirements (UBA, 2019). Care must be taken to ensure environmental safety of secondary P sources. For example, as mentioned in the introduction, untreated secondary P sources such as manure or sewage sludge carry high risks of contamination with heavy metals or pathogens (Harrison et al., 2006; Baize, 2009; Magri et al., 2019). Any additional processes utilized to alleviate such risks add to the cost of production (Egle et al., 2016). RockP-based fertilizers remain in general cheaper than the alternatives. However, over the last decade the price of RockP has increased dramatically and shows no sign of plateauing (IndexMundi, 2023). As outlined by UBA (2019) secondary P sources will become economically viable in the foreseeable future in the German market. Struvites are a promising alternative P source already in use in soil-based plant production. Struvites are highly plant available, environmentally safe and are already produced on an industrial scale (e.g. in the Netherlands). However, it must be stated that recovery of P from waste streams in the form of struvite is currently limited at around 50% (UBA, 2019). This currently limits the viability of struvites alone as major secondary P sources for horticultural plant production. Combining struvites with P extracted using other technologies will therefore be required for more widespread use of secondary P sources, including for plants grown in growing media. The research performed in the current studies is therefore highly valuable to growers.

5.2. Prediction of plant-available secondary source-P in soilless cultivation by growing media analyses.

Extraction methods (e.g., CAT- or CAL-method) are common growing media analyses to monitor plant-available nutrients, which support growers to adjust their fertilization management according to the plant demand during cultivation. For secondary source-P, various authors stated (Kratz et al., 2019; Duboc et al., 2022) that plant availability among different secondary P sources cannot be well characterized by a single extractant due to their extremely heterogenic P-bearing phase driving their plant P availability. This is in accordance with the observation of section I, where the combined approach (P_{mod}) of two commonly used growing media extraction methods to characterize plant-available P in growing media (CAL- and CAT-method) overcomes the limitations of each individual method. Here, P_{mod} was closely related to plant P uptake at trial end ($R^2 = 0.89$). Similar close relationships between P_{mod} and plant P uptake were obtained for pot trials of the other sections (section II: $R^2 = 0.83$, section III: $R^2 = 0.87$). However, not all trials were included in the evaluation of P_{mod}'s ability to reflect P taken up by plants. To complement the findings about P_{mod}'s ability to characterize plant-available secondary source-P, an assessment including all trial data, where the P supply was performed highly accurate (pot filling by weight) was carried out stepwise, starting with section I (Figure 11). For data sampling where the pool of plant available P in the growing media was not exhausted (in early stages of plant development), the sum of plant P (plant P uptake) and the residual plant-available P in the growing medium according to P_{mod} (residual P_{mod}) at trial end was compared with the estimated amount of plant-available P according in the growing medium at trial start (P_{mod}). As shown in Figure 11, only very small differences were observed between the two sampling time points (two and four weeks) for the sum of plant P uptake and residual amount of P_{mod}. This indicates that the characterization of the plant-available P pool in growing media fertilized with secondary P sources can be performed irrespectively from cultivation time or plant development. However, it has to be noted that under the more holistic evaluation of the P-pools in the plant-growing media system, the sum parameter of plant P uptake and residual P_{mod} after harvest are slightly higher compared to P_{mod} at trial start and thus led in most cases to points falling slightly above the bisector. This may indicate that the estimated P availabilities for some secondary P sources were conservative, and that actually slightly more P than estimated was plant available.

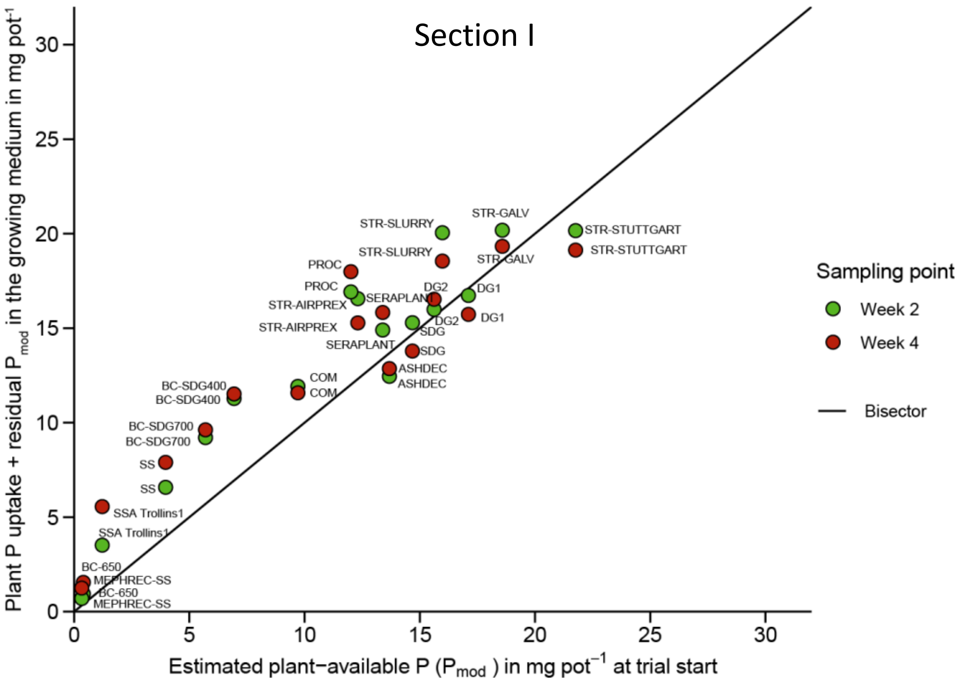

Figure 11: Relationship between the estimated plant-available phosphorus (P) in the growing medium at trail start (P_{mod}) and the sum of plant P uptake and the residual amount of P_{mod} in the growing medium at two harvesting dates (after two and four weeks of cultivation).

However, in both cases the points were near the bisector and thus such differences were not of practical relevance. For the plant availability of secondary source-P affected by the pH in the growing medium, P_{mod} could characterize the pool of plant-available P quite well for most secondary sources (Figure 12). However, the increased plant availability of SSAs derived municipal-wastewater was strongly underestimated. As already described in section II, this is attributed to the inability of the used solvents (CAT, CAL) to extract FeP or AlP, which was shown by Lohr et al. (2023) in detail. Consequently, to satisfactorily characterize plant availability of such secondary P-forms, there is a need for additional extractants, or solvent modifications. According to the pot trials investigating sewage sludge-based fertilizers, Handreck et al. (1996) showed that bicarbonate extractable-P is highly related to plant P uptake, and thus this might be a promising approach worth investigating for implementation in P_{mod}. However, is has to be noted that for one SSA (SSA_{Luenen}), the characterization of the plant availability was quite accurate by P_{mod}. Here it can be assumed that the plant availability might be partly driven by heavy metal associated P compounds such as PbP (Dorozhkin, 2011) or even uranium or thorium phosphates (Vogel et al., 2020), which might be reflected by P_{mod}.

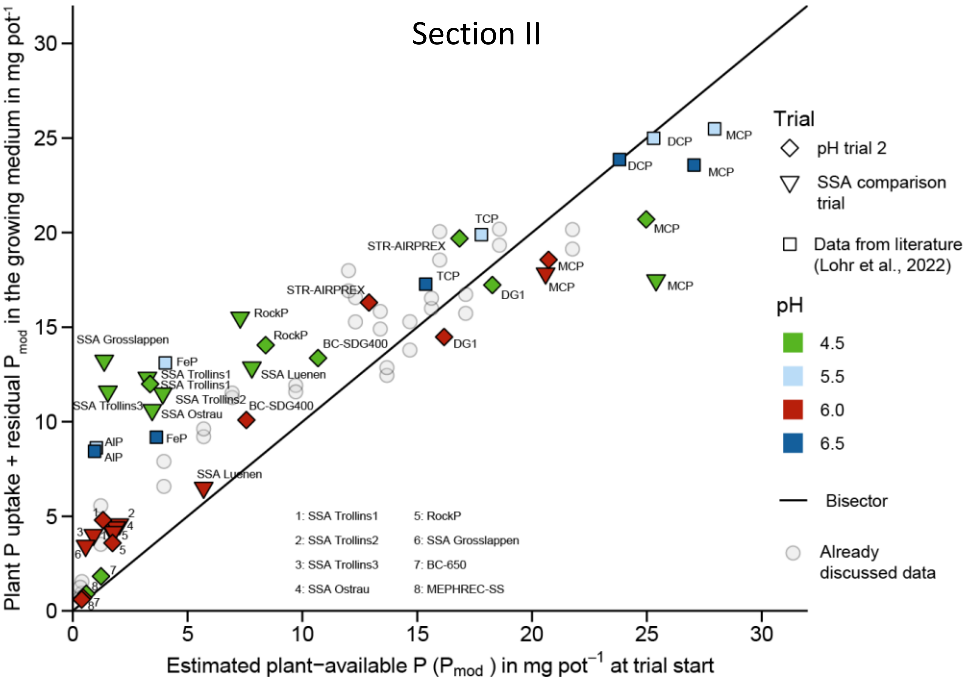

Figure 12: Relationship between the estimated plant-available phosphorus (P) in the growing medium at trail start (P_{mod}) and the sum of plant P uptake and the residual amount of P_{mod} in the growing medium at harvest for the trials in section II (pH trial 2, SSA comparison trial) at contrasting pH-level in the growing medium (4.5, 6.0). As benchmark, data for aluminum and iron phosphate (AlP, FeP) and three calcium phosphates of different crystallinity (mono-, di-, tri-calcium phosphate (MCP, DCP, TCP)), tested in a comparable trials set up (Lohr et al., 2023), were added.

Plant availability of RockP at pH 4.5 was slightly underestimated by P_{mod} values at trial start which was most obvious in SSA comparison trial. Since RockP consists mainly of apatite, which is highly soluble under acidic conditions, the CAT- and CAL-extractable amounts of P in the growing medium, and thus P_{mod}, were expected to be higher. For MCP-P, P_{mod} at trial start reflected the plant P uptake plus the residual P_{mod} at trial end quite well. However, this fit was for one MCP value less accurate (SSA comparison trial, pH 4.5) compared to the others and should be handled with caution. Data, where profound limitations were displayed, were discarded for the final evaluation of P_{mod}, and an outlier test (Cook`s distance) for regression analyses was performed for striking points.

As shown in Figure 13, most of the data for different grain sizes were located near the bisector. As such, the P_{mod} could reflect the effect of growing media grain size on the plant P availability of the tested secondary P sources. However, for the finest grind of sewage sludge-based BC-650, P_{mod} values were above the bisector due to lower P values found at the trial start than at the end. This underestimation of P_{mod} at trial start was comparable to the underestimation of municipal SSAs at a comparable growing media pH (Figure 12) and thus is not of practical relevance. However, due to a lack of variation in data and a small sample size, the findings about P_{mod}'s ability to characterize plant availability for secondary P sources of different grain sizes in the growing medium should be handled indicative only.

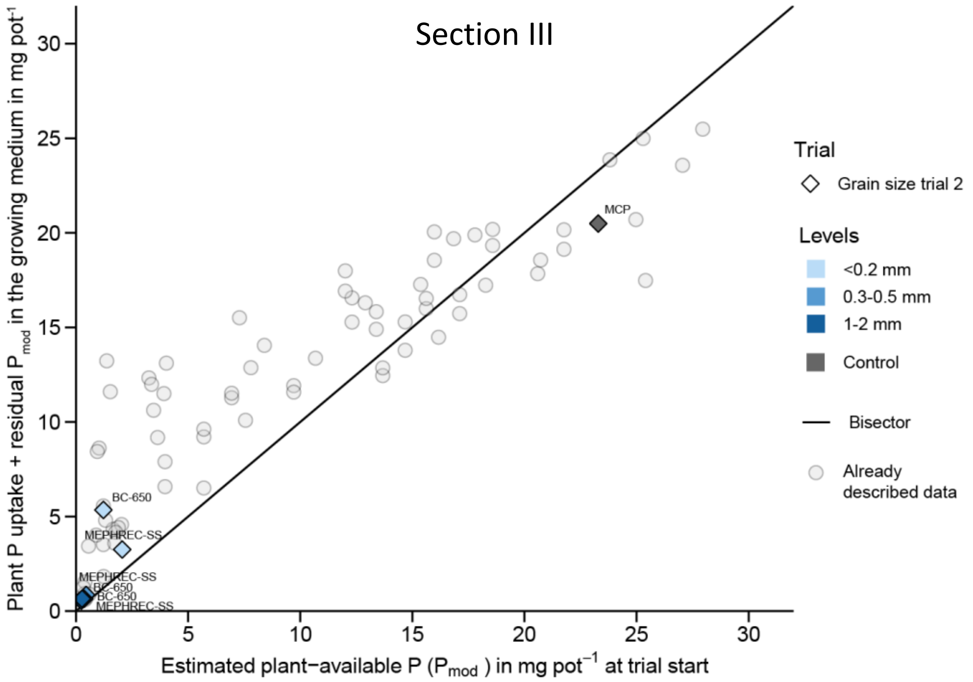

Figure 13: Relationship between the estimated plant-available phosphorus (P) in the growing medium at trail start (P_{mod}) and the sum of plant P uptake and the residual amount of P_{mod} in the growing medium at harvest for secondary P sources of different grain size are displayed.

As shown in Figure 14, the summarized sections data showed a close relation between P_{mod} at the beginning of the trial and the P uptake of the plant + the amount of P extractable at the end of the trial ($R^2 = 0.90$). Despite the outlined limitations for secondary P sources containing FeP or AlP, P_{mod} seems to be a promising approach to characterize plant-available secondary source-P in crop production using peat-based growing media.

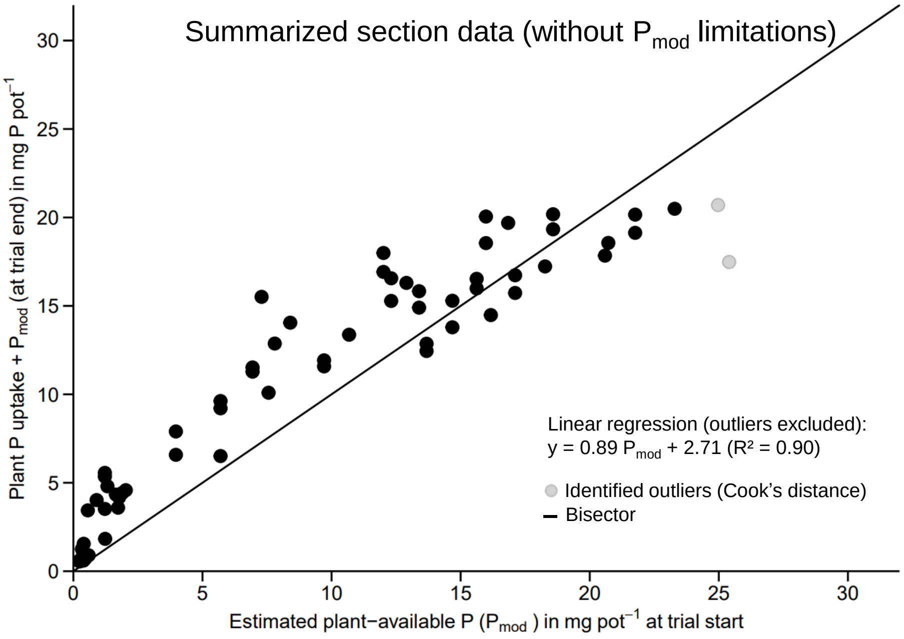

Figure 14: Relationship between the estimated plant-available phosphorus (P) in the growing medium at trail start (P_{mod}) and the sum of plant P uptake and the residual amount of P_{mod} in for all data (P_{mod} limitations excluded

However, it should be noted, that for smaller values (<10 mg P pot^{-1}) at trail start, P_{mod} tended to underestimate plant P availability of secondary source-P, since the data fall slightly above the bisector, while for higher P_{mod} values the opposite is apparent. This underestimation might be linked to presence of P compounds which are not or barely extractable by the solvents CAT or CAL, as already discussed in detail throughout this thesis. Alternatively, this might be an effect of the interaction with the model plant, changing actively the solubility of P sources with low plant-availability for example by exudation of acids (Xie et al., 2023).

As outlined in the introduction, the P dynamics in plant production systems are very complex. For the presented innovative approach of P_{mod} prediction of the plant availability of secondary P sources in growing media-based plant production, not much is known about the role of the cultivated plant and its interaction with growing media and secondary P sources. This implies the urgent need of additional experiments to improve the understanding of P_{mod}'s ability to characterize availability of secondary P sources to different plant species. Therefore, the presented well-correlating results for P_{mod}'s ability to predict plant availability of secondary source-P should be further validated with different crops, different secondary P sources and in multi-component growing media.

6. Conclusion

The investigated plant availability of secondary P sources for horticultural crop production differed between the secondary P sources and was further influenced by the pH in the growing medium and the fertilizers' particle size.

At a growing media pH of 6.0, which is tolerated by the most horticultural crops, the fertilization with secondary source-P led for the most cases to a comparable plant growth compare to the water-soluble reference fertilizer at trial end. However, only plants fertilized with struvite-P were able to reach similar plant P uptake compared to the control. Thus struvites might be the most promising substitutes for highly processed fertilizers derived from the finite reserves rock phosphate. For the rest of the secondary sources - except of two products - similar plant P uptake can be ensured by applying twice the amount of secondary source-P.

For crops cultivated under more acidic condition this amount can be reduced, since plant P availability increased at growing media pH <5. However the enhancement of plant P availability varied between the tested secondary P sources and was the highest for the sewage sludge ashes. According to studies, 1.3 of the reference fertilizers amount should ensure comparable plant P uptake if secondary P sources are applied as powder form. However, to ensure the optimal plant P availability of the secondary source, the grain size must be considered. Providing the secondary P source as fine power is recommended, since a reduction in plant P availability can be assumed if coarser particles are applied.

The new approach combining CAT- and CAL-extractable P in the growing medium reflected the plant availability of secondary source-P quite well. However, this new approach could not satisfactorily characterize the plant P availability of iron or aluminum phosphates under acidic conditions in the growing media. This implies the urgent need of further research to satisfactorily characterize plant availability of secondary source-P in growing media, which can help growers to adjust their fertilization management according to the plant demand.

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Appendix

List of scientific contributions

Peer-reviewed publications

Lohr, D., Babel, B., Lau, C., Levaillant, N., Prell, F., Hauck, D., 2023: Estimation of plant availability of different phosphates by the $CaCl_2$/DTPA and CAL method. Acta Horticulturae 1377, 777-784. https://doi.org/10.17660/ActaHortic.2023.1377.96

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Poster presentations

Hauck, D.; Lohr, D.; Max, J.; Meinken, E., 2021: Plant availability of phosphorus in recycled fertilizers from wastewater treatment - effect of grain size. At Growing Media, - International Symposium on Growing Media, Soilless Cultivation, and Compost Utilization in Horticulture, 22.-27.08.2021, Ghent, Belgium.

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