Alternative phosphorus resources from urban waste as fertilization

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List of Acronyms

AM	Arbuscular mycorrhizae
ANOVA	Analysis of variance
CA	Citric acid
CAL	Calcium-acetate-lactate
DGT	Diffusive gradient in thin films
DM	Dry matter
EU	European Union
FM	Fresh matter
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
LCA	Life cycle assessment
NAC	Neutral ammonium citrate
P	Phosphorus
P_{CAL}	Concentration of phosphorus extracted by calcium-acetate-lactate
P_{NAC}	Concentration of phosphorus extracted by neutral ammonium citrate
^{31}P-NMR	Phosphorus-31 nuclear magnetic resonance
POP	Persistent organic pollutants
PUE	Phosphorus use efficiency
SSA	Sewage sludge ash

1. Summary – Zusammenfassung

1.1 Summary

Phosphorus (P) is an essential macronutrient for plants. Plant roots assimilate P in soil mainly in the form of orthophosphates as $H_2PO_4^-$ and HPO_4^{2-}. Due to the high reactivity, orthophosphates generally exist at low concentrations in soils that have high P sorption capacity. Besides the indigenous P in soil, fertilizers manufactured from phosphate rock are the main source of P to ensure a satisfactory yield in agricultural production. However, phosphate rock is a limited reserve with uneven quality and is geographically restricted. Technologies for recovering and reusing the P from waste streams were therefore developed to alleviate the dependency on this critical raw material and to promote sustainable solutions. Sewage sludge, which contains most of the P from wastewater, has great potential to produce P-rich products. However, the evaluation of their P availabilities to plants by simple chemical extraction of the product is difficult because they often contain different P species that do not easily dissolve in water. In the first chapter, three types of recycled P fertilizers derived from sewage sludge were tested first in the greenhouse using maize in two different substrates and were incubated in soil for 0, 22, and 56 days. Untreated sewage sludge ash (SSA), Na-treated SSA, and struvite were tested here. Untreated SSA failed to promote the growth of young maize, while Na-treated SSA and struvite achieved similar biomass as mineral P fertilizer. The pre-incubation time had a negative impact on the P use efficiency of recycled fertilizers. Although the P availability of untreated SSA was very low, it might be a potential substitute for phosphate rock to produce fertilizers. In Chapter II, the P availability and heavy metal contamination risk of superphosphate produced with untreated SSA in the lab were investigated. It was found that the superphosphate produced with the mixture of 25% SSA and 75% rock phosphate had a similar P use efficiency as the superphosphate produced with 100% rock phosphate, indicating untreated SSA could be a suitable substitution of rock phosphate in the P fertilizer production. Despite the heavy metal accumulations in soil and plant being minimal, the Pb and Cu concentration in untreated SSA exceeded the maximum limit according to the EU regulation on fertilizers and therefore its use is restricted in fertilizer production. The separation of industrial and municipal sludge before incineration is recommended to obtain SSAs with high P concentrations but less heavy metal.

In Chapter III, the P availability of granulated struvite as affected by fertilizer application methods in comparison to di-ammonium phosphate (DAP) was investigated under field conditions. The experiment was conducted in one field in 2020 and repeated in an adjacent field in 2021. Two-year maize results showed an increase of 30% in maize yield and P content when struvite was placed, indicating that fertilizer placement enhanced the efficiency of granulated struvite. Struvite-placed had similar P use efficiency as DAP-placed, and both treatments led to significantly higher yield and P content of maize than no-P control. The residual effect of fertilizer treatment was evaluated with faba bean (*Vicia faba*) and triticale (*Triticosecale Wittm. ex A. Camus.*) as subsequent crops after maize. No significant difference in yield and P content was found between struvite-placed and DAP-placed. Nevertheless, this chapter demonstrated that placed struvite can replace DAP as P fertilizer in maize cultivation.

In Chapter IV, the sensitivity of three P extraction methods to different P species was investigated to provide insights into the characterization of current soil P tests to plant P availability. Three soil P tests were compared: calcium acetate-lactate (CAL), Olsen, and

diffusive gradients in thin films (DGT). Results showed that a portion of added orthophosphates was immediately fixed in the soil and cannot be extracted by any of the methods. The acidic CAL method may overestimate immediately plant-available P of insoluble calcium phosphate like $Ca_3(PO_4)_2$. The most suitable method to determine immediately available P might be the Olsen and DGT method.

To conclude, this dissertation demonstrated the P availability of recycled P fertilizers derived from sewage sludge and possible strategies to enhance their P use efficiencies. It provided agronomic evidence on the feasibility of replacing phosphate rock-derived P fertilizers with recycled fertilizers and insight into its land application. With the recently revised EU regulation on fertilizing products, it can be expected that recycled fertilizers will soon share the market with mineral fertilizers and help develop sustainable agriculture.

1.2 Zusammenfassung

Phosphor (P) ist ein wesentlicher Makronährstoff für das Wachstum und die Entwicklung von Pflanzen. Pflanzenwurzeln assimilieren P im Boden hauptsächlich in Form von Orthophosphaten wie $H_2PO_4^-$ und HPO_4^{2-}. Aufgrund der hohen Reaktivität liegen Orthophosphate in Böden, die eine hohe P-Sorptionskapazität haben, oft in geringen Konzentrationen vor. Neben dem bodeneigenen P sind aus Phosphorit hergestellte Düngemittel die wichtigste P-Quelle, um einen zufriedenstellenden Ertrag in der landwirtschaftlichen Produktion zu gewährleisten. Rohphosphat ist jedoch eine begrenzte Reserve mit uneinheitlicher Qualität und geografisch sehr ungleich verteilt mit nur geringen Vorkommen in Europa. Technologien zur Rückgewinnung und Wiederverwendung von P aus Abfallströmen wurden entwickelt, um die Abhängigkeit von diesem wichtigen Rohstoff zu verringern und nachhaltige Lösungen zu fördern. Klärschlamm, der den größten Teil des P im Abwasser enthält, hat ein großes Potenzial zur Herstellung von P-reichen Produkten. Die Bewertung ihrer P-Verfügbarkeit für Pflanzen durch einfache chemische Extraktion des Produkts ist jedoch schwierig, da sie oft verschiedene P-Fraktionen enthalten, die sich nicht leicht in Wasser auflösen. Im ersten Kapitel wurden drei Arten von recyceltem P-Dünger aus Klärschlamm zunächst im Gewächshaus mit Mais in zwei verschiedenen Substraten getestet und 0, 22 und 56 Tage lang im Boden bebrütet. Hier wurden unbehandelte Klärschlammasche (SSA), Na-behandelte SSA und Struvit getestet. Unbehandeltes SSA förderte das Wachstum von jungem Mais nicht, während mit Na-behandeltem SSA und Struvit eine ähnliche Biomasse erreicht wurde wie mit mineralischem P-Dünger. Die Vorinkubationszeit wirkte sich negativ auf die P-Nutzungseffizienz der recycelten Düngemittel aus. Obwohl die P-Verfügbarkeit von unbehandeltem SSA sehr gering war, könnte es ein möglicher Ersatz für Rohphosphat zur Herstellung von Düngemitteln sein. In Kapitel II untersuchten wir die P-Verfügbarkeit und das Risiko einer Schwermetallverunreinigung von Superphosphat, das mit unbehandeltem SSA im Labor hergestellt wurde. Wir fanden heraus, dass das mit einer Mischung aus 25 % SSA und 75 % Rohphosphat hergestellte Superphosphat fast die gleiche P-Nutzungseffizienz aufwies wie das mit 100 % Rohphosphat hergestellte Superphosphat, was darauf hindeutet, dass unbehandeltes SSA ein geeigneter Ersatz für Rohphosphat in der P-Düngerproduktion sein könnte. Obwohl die Anreicherung von Schwermetallen im Boden und in den Pflanzen minimal war, überstieg die Pb- und Cu-Konzentration in unbehandeltem SSA den Höchstwert gemäß der EU-Düngemittelverordnung, so dass seine Verwendung in der Düngemittelproduktion eingeschränkt ist. Die Trennung von Industrie- und

Kommunalschlämmen vor der Verbrennung wird empfohlen, um SSA mit hohen P-Konzentrationen, aber weniger Schwermetallen zu erhalten.

In Kapitel III untersuchten wir die P-Verfügbarkeit von granuliertem Struvit im Vergleich zu Diammoniumphosphat (DAP) unter Feldbedingungen in Abhängigkeit von der Art der Düngung. Der Versuch wurde im Jahr 2020 auf einem Feld durchgeführt und 2021 auf einem benachbarten Feld wiederholt. Die Ergebnisse für zweijährigen Mais zeigten eine Steigerung des Maisertrags und des P-Gehalts um 30 %, wenn Struvit unterfußdüngt wurde, was darauf hindeutet, dass die Unterfußdüngung von Dünger die Effizienz von granuliertem Struvit erhöht. Bei der Unterfußdüngung, hatte Struvit eine ähnliche P-Nutzungseffizienz wie DAP, und beide Behandlungen führten zu einem signifikant höheren Ertrag und P-Gehalt von Mais als die Kontrolle ohne P. Der Residualeffekt der Düngerbehandlung wurde mit Ackerbohne (*Vicia faba*) und Triticale (*Triticosecale Wittm. ex A. Camus.*) als Folgekulturen nach Mais untersucht. Es wurde kein signifikanter Unterschied im Ertrag und P-Gehalt zwischen Struvit- und DAP-Düngung festgestellt. Dennoch hat dieses Kapitel gezeigt, dass unterfußdüngtes Struvit DAP als P-Dünger im Maisanbau ersetzen kann.

In Kapitel IV wurde die Empfindlichkeit von drei P-Extraktionsmethoden gegenüber verschiedenen P-Fraktionen untersucht, um Einblicke in die Vorhersage aktueller Boden-P-Tests zur P-Verfügbarkeit in Pflanzen zu erhalten. Drei Boden-P-Tests wurden verglichen: Calciumacetat-Lactat (CAL), Olsen und Diffusionsgradienten in dünnen Schichten (DGT). Die Ergebnisse zeigten, dass ein Teil der zugesetzten Orthophosphate sofort im Boden fixiert wurde und mit keiner der Methoden extrahiert werden kann. Die Extraktion mit der sauren CAL-Lösung kann den unmittelbar pflanzenverfügbaren P von unlöslichem Kalziumphosphat

wie $Ca_3(PO_4)_2$ überschätzen. Die geeignetste Methode zur Bestimmung des unmittelbar verfügbaren P dürfte die Olsen- und DGT-Methode sein.

Zusammenfassend lässt sich sagen, dass diese Dissertation die P-Verfügbarkeit von rezyklierten P-Düngern aus Klärschlamm und mögliche Strategien zur Verbesserung ihrer P-Nutzungseffizienz aufgezeigt hat. Sie lieferte agronomische Beweise für die Durchführbarkeit des Ersatzes von aus Phosphorit gewonnenen P-Düngern durch rezyklierte Düngemittel und neue Erkenntnisse über deren Ausbringung. Mit der kürzlich überarbeiteten EU-Verordnung über Düngemittel ist zu erwarten, dass recycelte Düngemittel bald den Markt mit Mineraldüngern teilen und zur Entwicklung einer nachhaltigen Landwirtschaft beitragen werden.

2. Introduction

2.1 Sustainability challenges of global phosphorus resources and coping strategy adopted in the European Union

Phosphorus (P) is one of the essential nutrient elements for plant growth and development. It involves the formation of nucleic acids, phospholipids of bio-membranes, and it also plays a vital role in metabolic energy transfer in cells as phosphate esters and energy-rich phosphate compounds (*Hawkesford* et al., 2012). In soil, naturally occurring P is restricted by the releasing rate of P minerals during soil weathering. Plants take up P as inorganic orthophosphates ($H_2PO_4^-$/HPO_4^{2-}), which are highly reactive and therefore exist in soil solutions at low concentrations (*Lal* and *Stewart*, 2016). The typical range for orthophosphates in arable soil solution in temperate humid climates is from 0.4-40 mg L^{-1} (*Blume* et al., 2016). To meet the nutrient requirement of plants, P fertilizers are often applied in low-P soil together with other macronutrients. These fertilizers are designated to be highly soluble in water to provide sufficient P to plant immediately after being applied to the soil.

As the world's population keeps growing, which is projected to be around 9.7 billion in 2050 (*United Nations* et al., 2019), the demand for P fertilizer may also increase to produce enough food. Moreover, the change in people's diet could also influence the demand. A rough calculation showed that the meat-based diet requires 180% more phosphate rock compared to the vegetable-based diet (*Cordell* et al., 2009), which could become a relevant issue in developing countries with rapid growth, where more people can afford a meat-based diet. The world P demand for fertilizer purposes has been gradually increasing since 2016 (*Food and Agriculture Organization*, 2019). In the meantime, natural phosphorus resources are depleting and the remaining reserves show a reduced quality (*Kratz* et al., 2016; *Van Kauwenberg*, 2010). Mineral phosphate fertilizers are manufactured from phosphate rock, a raw material that is non-renewable, non-substitutable, and geographically restricted. The world reserves of phosphate rock are mainly located in Morocco and Western Sahara, China, and Algeria (*U.S. Geological Survey*, 2020). The geopolitical constraints related to the P reserves are predicted to become worse in the future, causing limited access to P fertilizer for farmers in many countries (*Chowdhury* et al., 2017).

For areas with limited phosphate rock reserves, like Europe, alternative P sources are important to alleviate the dependency on the import of phosphate rock. Around 84% of phosphate rock demand in the EU relied on imports from 2012 to 2016 (*European Commission*, 2020). A 5-R strategy was therefore proposed, including re-aligning P inputs to match requirements, reducing P losses to water, recycling P in bioresources, recovering P in waste, and redefining P in the food systems (*Withers* et al., 2015). Implementing the use of secondary P raw materials, like animal manure, wastewater, and food waste as fertilizer and enhancing the efficiency of fertilizer are possible solutions. The EU's revised Waste Framework Directive has set targets for the re-use and recycling of at minimum 55% of municipal waste by 2025. The Circular Economy Action Plan adopted by the European Commission also promotes the use of sustainable resources and encourages the revision of the Fertilizer Regulation to include products from waste streams in the fertilizer market. As a result, three recycled secondary materials are included in the 'component material category' in the EU Fertilising Products Regulation ((EU) 2019/1009): precipitated phosphate salts and derivate, thermal oxidation materials, and derivate, pyrolysis and gasification materials

(*Huygens* et al., 2019), enabling the legal use of resources from waste as fertilizer in agricultural production.

2.2 Recycling and recovering P: from sewage sludge to agricultural land

While the limited reserves of phosphate rock might pose a risk to future food security, substantial P was lost during the consumption and production of food and non-food product. It was shown that in 2005, 1,217 thousand tonnes of P was lost from the production-consumption system in the EU, which accounted for half of the net trade P-balance (*van Dijk* et al., 2016). Around 30% of the total P losses ended up in wastewater systems through the consumption sector, which could reduce 26% of total import P for crop production (*van Dijk* et al., 2016). Several access points of potential P recovery during and after the wastewater treatment process were concluded in Figure 1 (*Egle* et al., 2015), where only sewage sludge and sewage sludge ash have P recovery potentials over 90%. The fate of sewage sludge includes agricultural use, compost, landfill, incineration, and others. Around one-third of the discarded sludge in the EU is used in agriculture and incineration respectively (Figure 2).

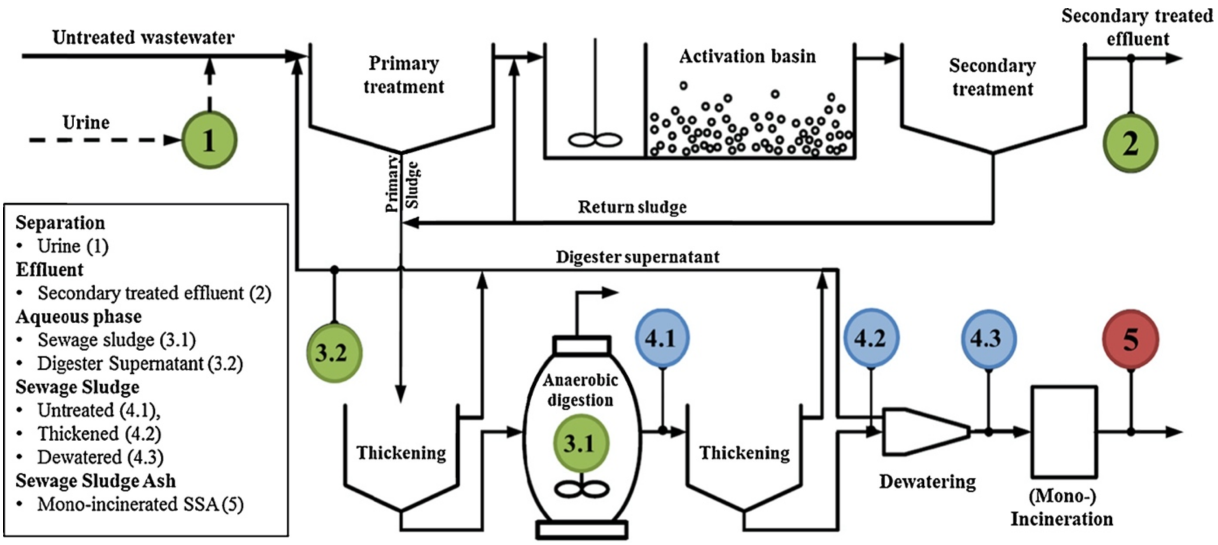

Figure 1. Potential access points for P recovery approaches during and after wastewater treatment (Egle et al., 2015).

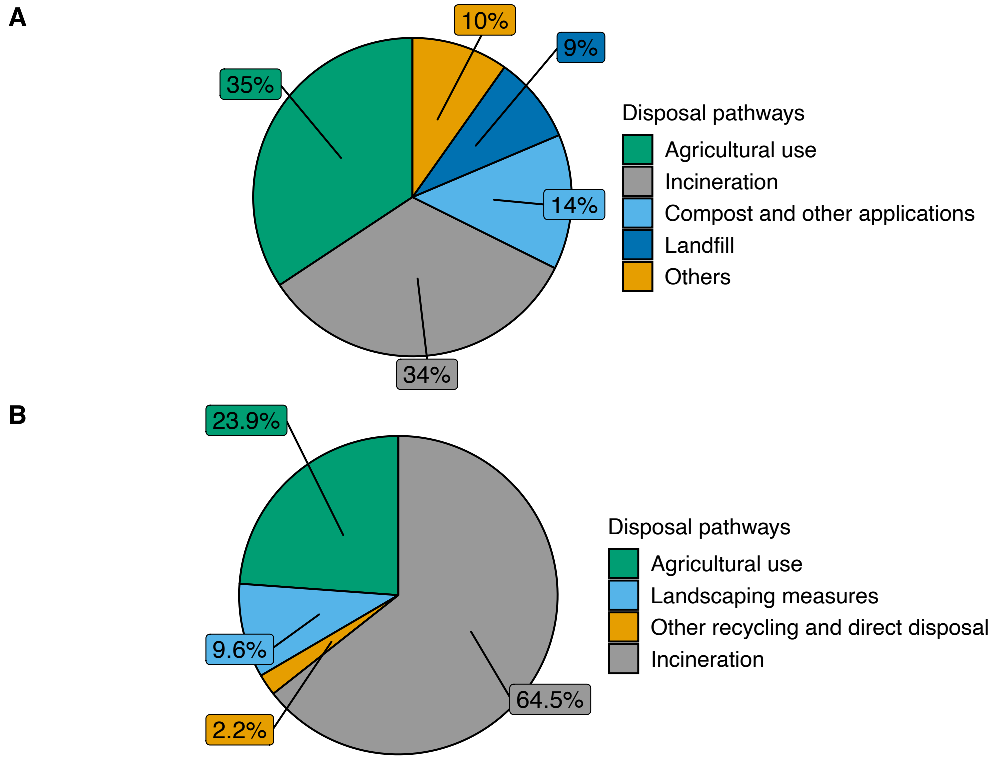

Figure 2. Percentage distribution of disposal pathways of sewage sludge in the Europe Union (A) and in Germany (B) in 2016. Data from (*Eurostat*, 2021; *Roskosch* and *Heidecke*, 2018).

Except for agricultural use and compost, the rest of the disposal ways remove the P in the sewage sludge from the system as losses. To recover and recycle P from this loss, various technologies have been developed in recent years. In Germany, two-thirds of the sewage sludge were discarded via incineration (Figure 2), including co-incineration and mono-incineration. During co-incineration, the sludge is incinerated together with coal, waste, or cement materials, while during mono-incineration the sludge is solely incinerated and produces sewage sludge ash (SSA) as the end product (*Roskosch* and *Heidecke*, 2018). Around half of the sludge incineration in Germany occurs in mono-incineration plants, which ends up eventually in landfill, mine filling, or for construction purposes (*Krüger* et al., 2014). However, SSA contains a median P content of 7.9% which should not be neglected and regarded as a waste (*Krüger* et al., 2014). The benefit of using SSA as the secondary P source is that all P in the sludge is concentrated due to mass reduction which makes it easy to transport. Furthermore, organic pollutants in the sludge are almost completely oxidized during the combustion (*Deng* et al., 2009) together with pathogens and microorganisms.

The thermal conversion processes of sewage sludge determine the quality of SSA as P fertilizer. In Germany, there are 29 mono-incineration plants and 1 mono-gasification plant treating municipal and industrial sewage sludge in 2018 where most of the mono-incineration plants are equipped with stationary fluidized bed technology (*Roskosch* and *Heidecke*, 2018). Phosphate is thermally stable during incineration at 800-900 ºC and is concentrated in the SSA as whitlockite-type tri-calcium phosphate, which is not immediately available for plants (*Donatello*, 2013). Aluminum or iron phosphate can also be present in the SSA due to the P-removal process in wastewater treatment. A study on SSAs produced from incineration, pyrolysis and gasification found that pyrolyzed SSA had the most readily available P species from municipal sewage sludge than the other two thermal conversions (*Thomsen* et al., 2017). They further suggested a post-oxidation of pyrolyzed ash to reduce the sparingly soluble P pools and form more plant-available P species which is in association with Mg. Other post-treatment technologies were developed to enhance the P availability of the SSA. For instance, the Cl-donor was mixed with SSA at a temperature of 1000 ºC to remove heavy metals and to form Ca- and Mg-bearing phosphates which were largely soluble in citric acid (*Adam* et al., 2009). Further, they improved it to the AshDec® process which mixes SSA with alkaline Na-containing compounds (like Na_2SO_4) at a temperature over 900ºC to produce a Rhenania phosphate-like compound with a reduced content of heavy metals (*Hermann* and *Schaaf*, 2019).

Besides post-treatment of the SSA, extracting P from the SSA is another recovery route. Bioleaching, wet-chemical extraction, and leaching with acid or base are applied to SSA to produce P-rich biomass, single superphosphate, phosphoric acid, or phosphate salts (*Donatello* et al., 2010; *Egle* et al., 2015; *Lim* and *Kim*, 2017; *Mochiyama*, 2019). To meet the requirement regarding heavy metal content in the fertilizer according to the EU and local regulations, post-treatment processes of SSA often include an effective heavy metal-removal step before delivering the final product.

In Germany, P in the sludge which is not incinerated can also be recovered and reused as P fertilizer (Figure 2). Most of the approaches that recover P from sludge contain processes of P dissolution, removal of heavy metals and interfering ions, filtration, and phosphate precipitation (*Egle* et al., 2015). Among different phosphate precipitates, struvite-containing precipitation products are often regarded as effective P fertilizers. The main P species in these products is struvite ($MgNH_4PO_4 \cdot 6H_2O$), but they can contain other compounds like brushite and dittmarite. Currently, there are 19 different technologies to produce struvite from sludge or wastewater treatment from the agricultural industry (mainly in food processing) (*Shaddel* et al., 2019). The highlight of struvite as P fertilizer is its similar or even higher efficiency compared to traditional phosphate rock-derived fertilizer based on numerous pot studies (*Hertzberger* et al., 2020). In the meantime, many factors have a significant impact on the fertilizer efficiency of struvite, such as soil pH, soil plant-available P, plant species, the application rate, and its granule size (*Hertzberger* et al., 2020; *Talboys* et al., 2016; *Vogel* et al., 2015). Struvite is considered a slow-release P fertilizer because of its low water solubility. Therefore, it is often questionable for struvite to supply sufficient phosphorus to plants at the early stage. Blending struvite with waster-soluble P fertilizer is recommended to ensure a consistent P supply during plant growth (*Hertzberger* et al., 2021). It was also found that with the help of arbuscular mycorrhizae (AM) colonization, struvite resulted in higher shoot biomass, P and N content of tomato than mono ammonium phosphate (*Di Tomassi* et al., 2021). Overall, various P recovery technologies are implemented at pilot-/full- scale together with in-depth studies on their products, which fulfills the objective of recycling P in bioresources more effectively to substitute inorganic fertilizer consumption in the 5R strategy to reduce the EU's dependency on P import.

2.3 Challenges of recycled products as P fertilizer: contamination risk and P bioavailability

One of the most concerns about using fertilizers recycled from waste streams in agricultural production is the contamination risk, including heavy metal contamination and organic pollutant contamination. SSAs contain the heavy metals from sewage sludge, as some of them don't completely volatilize during the combustion at 800-900 ºC and are therefore concentrated in SSAs. If compared with commercial rock phosphate in Germany, SSAs produced from German sludge had a higher concentration of Pb, Ni, As, Cu, and Zn, where some exceeded the maximum limit in the EU fertilizer regulation (Table 1). Although the Cd concentration in SSAs is lower than it is in rock phosphate, the post-treatment with heavy metal removal or the separation of industrial and municipal sewage sludge before the combustion is required to legally place SSA on the fertilizer market. Besides, if compared to phosphate fertilizers that are produced by phosphoric acid (like mono-/di-ammonium phosphate), SSAs would contain much higher heavy metal concentrations. However, SSAs are less associated with organic pollutants than heavy metals, since almost all organic matter is oxidized during combustion.

As a participating product, struvite has a smaller risk of heavy metal contamination than SSAs. Two surveys of struvite produced in the Netherlands and the EU showed none of the struvite samples exceeded the heavy metal concentration limit according to Dutch and EU regulations (*Gell* et al., 2011; *Muys* et al., 2021). The same result was found for pathogens and indicator organisms. Regarding organic pollutants, some studies found the struvite from urine was free of pharmaceuticals (*Ronteltap* et al., 2007; *Schürmann* et al., 2012). For persistent organic pollutants like polycyclic aromatic hydrocarbons, analysis is needed before the use of struvite in agriculture.

Table 1. The mean concentration of trace elements in sewage sludge ashes (SSA) and soft ground rock phosphate in Germany and their threshold values (mg kg^{-1} dry matter) defined by the German Fertilizer Ordinance (DüMV) and the European Union fertilizer regulation 2019/1009 (EU regulation). Data from (*Düngemittelverordnung*, 2012; *European Commission*, 2022; *Kratz* et al., 2016; *Krüger* et al., 2014).

	SSA	Rock phosphate	DüMV	EU regulation
Cd	2.7 mg kg^{-1} P_2O_5	46.2 mg kg^{-1} P_2O_5	50 mg kg^{-1} P_2O_5	60 mg kg^{-1} P_2O_5
Cr ^{VI}	-	-	2	2
Hg	0.8	-	1	1
Ni	105.8	22	80	100
Pb	117	6.9	150	120
As	17.5	8.3	40	40
Cu	785	15.1	-	600
Zn	2534	239	-	1500

The P bioavailability of recycled fertilizers varies between different types and production processes, which depends on the P speciation contained in the product. SSAs were reported to have extremely low P availability to plants due to the large share of sparingly soluble P forms (*Vogel* et al., 2017a). SSAs with post-treatment contain more readily labile and soluble P than SSAs, showing P bioavailability relatively close to water-soluble phosphate fertilizers, especially in acidic soils (*Nanzer* et al., 2014; *Vogel* et al., 2018, 2015, 2017a). Struvite is soluble in organic acids, showing similar or even higher P bioavailability than water-soluble P fertilizers in various greenhouse studies (*Hertzberger* et al., 2020). Although some argued that struvite is not able to supply sufficient P to plant at the early stage when in granular form due to a slow P diffusion (*Degryse* et al., 2017; *Hertzberger* et al., 2021; *Talboys* et al., 2016), the yield and P use efficiency at harvest were equivalent to water-soluble diammonium phosphate (*Talboys* et al., 2016). The P use efficiency (PUE) mentioned in this study is an indicator to evaluate the efficiency of P fertilizers in pot and field studies. It is the percentage of how much P from fertilizers is taken up by the plant:

$$PUE\ (\%) = \frac{\text{P content (treatment)} - \text{P content (Zero P control)}}{\text{Fertilized P}} \times 100$$

The short time of plant growth in the greenhouse may not be able to reflect the P bioavailability of struvite in a growing season. To date, only a very few published studies on struvite were conducted under field conditions (*Hertzberger* et al., 2020; *Vogel* et al., 2017b; *Wollmann* and *Möller*, 2018) and their results could not be concluded. To reach a better understanding of struvite as the substitution of phosphate rock-derived P fertilizer, the investigation of its P bioavailability under field conditions is crucial to real-life practice.

2.4 Reducing P overuse in agriculture: characterization of soil available P

Another objective in the 5R strategy is re-aligning P inputs to match actual P requirements. The restriction of P overuse in agriculture is addressed to reduce unnecessary P import and losses to water, further minimizing the risk of eutrophication (*Withers* et al., 2015). The determination of an appropriate fertilization rate is therefore critical to avoid over-fertilization. The fertilization rate is often recommended based on the soil P test, estimated crop P removal, previous crop, and other factors. Several routine soil P tests are applied to characterize the soil's available P status in the fertilization recommendation. For example, calcium-acetate-lactate (CAL) extraction is mainly adopted in Germany and Austria, while Olsen extraction is the standard soil P test in China. These tests extract distinct soil P pools to a different extent using extractants that have a range of pH from 1 to 8.5 (*Wuenscher* et al., 2016). The principle of the soil P test includes exchanging phosphate ions from surface adsorption with excessive organic/inorganic ions, reducing the concentration of cations like Al, Fe, and Ca that can actively bind phosphate ions, and dissolving insoluble phosphates (*Wuenscher* et al., 2016). Due to the different mechanisms in soil P tests, their results are difficult to be compared with each other. A study on the relationship between various soil P tests and plant P uptake showed that weak extraction (especially neutral salt solutions) of soil P correlated stronger with plant P than strong extraction, and this correlation was affected by soil textures (*Franz* et al., 2018). Weak extraction like water extraction determines immediately available and accessible phosphate for the plant in the soil solution, but it does not account for P that might be gradually available during the growing season. A fertilization recommendation based on weak soil P tests may result in a higher fertilization amount than the actual need of the plant and cause P loss via surface runoff and accumulating legacy P in the soil. However, strong extraction with a very low pH environment may overestimate the P that is available to the plant and the recommendation fails to meet the plant's requirement. A critical research question of sustainable P use lies in the appropriate soil P test for fertilization recommendation. This challenge promoted advanced progress in the application of novel soil P tests. The application of spectroscopic and spectrometric methods to P speciation has been investigated, like ^{31}P-NMR spectroscopy and high-resolution mass spectrometry (*Kruse* et al., 2015). Method like diffusive gradient in thin films (DGT) method was also investigated for the determination of soil available P by assessing the soil P diffusion (*Zhang* et al., 2013). In an investigation of 35 wheat field trails, the DGT method gave a better prediction of yield response to different P supplies than routine soil P tests (Colwell and resin method) regardless of soil type and was not substantially affected by climatic seasons, sowing time, and wheat varieties (*Mason* et al., 2010). It showed the great potential of the DGT method as a soil P test for fertilizer recommendation. Therefore, the comparison between the DGT method and widely applied soil P tests (like CAL and Olsen) is imperative to be investigated for a better characterization of soil available P.

2.5 Maize: one of the world’s leading staple cereals

Maize (*Zea mays* L.) is a major source of animal feed and human consumption. The global production of maize (dry grain) reached 1.2 billion tonnes in 2020, mainly in the United States and Asia (*Food and Agriculture Organization*, 2022). It is estimated to be the most widely cultivated and traded crop in the coming decade (*Erenstein* et al., 2022). In the meantime, deficient P in soils could be a limiting factor for the maize yield, especially in areas where the soil has a strong P sorption (*van der Velde* et al., 2014). Phosphorus is critical for maize in early development, influencing the leaf area, leaf appearance, elongation rate, and the aboveground biomass (*Plenet* et al., 2000). Therefore, in this dissertation, maize was utilized to evaluate the P fertilizing effect of recycled P fertilizers produced from urban waste both in the early stage and in the final stage. It is practical to investigate new types of fertilizers with a crop that is produced and consumed widely around the world.

2.6 Aims and objectives

Against the background of high dependency on P import in the EU, P recycling and recovering from wastewater have great potential to substitute parts of the P demand, especially in agriculture. This work aims to evaluate the P availability of various recycled P fertilizers derived from wastewater and to investigate means to increase their efficiencies both under controlled conditions and field conditions.

The specific objectives are:

- Evaluating the P availability of recycled P fertilizers from wastewater at the early stage of maize growth in two different soils and investigating the effect of incubation time on the P availability of recycled P fertilizers
- Assessing the P availability of superphosphate produced by rock phosphate and sewage sludge ash and investigating the heavy metal contamination risks
- Investigating the yield of maize and P use efficiency of struvite fertilization in the field and the effect of fertilizer application on its efficiency
- Analyzing the sensitivity of a diffusion soil P test compared to routine soil P tests with three calcium phosphate species in soils with different pH in an incubation experiment

Based on the objectives, the hypotheses in this dissertation are:

(1) the effectiveness of recycled P fertilizers differs and is affected by the incubation time by comparing their P use efficiency.

(2) SSA can partially substitute rock phosphate in superphosphate production while maintaining the same plant growth and nutrient uptake without enhanced heavy metal contamination in plants.

(3) Under fertilizer placement, struvite results in a similar yield of maize and P use efficiency as di-ammonium phosphate in the field.

(4) Plant-available P in fertilized soils is best characterized by the extraction method that does not disturb the chemical equilibrium in the soil-solution mixtures.

2.7 Structure of the dissertation

Besides the general introduction, discussion, and conclusion, this dissertation includes four sections corresponding to the objectives and hypotheses stated in section 2.6. Chapter I is a manuscript in preparation. Chapter II and Chapter IV are original research manuscripts that have been published in peer-reviewed journals. Chapter III is a manuscript submitted to a peer-reviewed journal.

Chapter I

Yawen You; Tobias Edward Hartmann; Torsten Müller. Effectiveness of recycled product from sewage sludge as P fertilizer and its characterization by chemical extractions. (In preparation).

Chapter II

Yawen You; Jakob Klein; Tobias Edward Hartmann; Peteh Mehdi Nkebiwe; Huaiyu Yang; Wei Zhang; Xinping Chen; Torsten Müller (2021). Producing superphosphate with sewage sludge ash: assessment of phosphorus availability and potential toxic element contamination. Agronomy 2021, 11, 1506. https://doi.org/10.3390/agronomy11081506

Chapter III

Yawen You; Tobias Edward Hartmann; Peteh Mehdi Nkebiwe; Torsten Müller. Yield Response of Maize as Affected by Struvite Placement and Residual Effects on Subsequent Crops. Submitted to Agronomy Journal.

Chapter IV

Tobias Edward Hartmann; Iris Wollmann; **Yawen You**; Torsten Müller (2019). Sensitivity of three phosphate extraction methods to the application of phosphate species differing in immediate plant availability. Agronomy 2019, 9, 29. https://doi:10.3390/agronomy9010029

3. Chapter I

Effectiveness of recycled product from sewage sludge as P fertilizer and its characterization by chemical extractions

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In preparation.

Abstract

Purpose: The application of P-containing products recycled from wastewater streams as P fertilizers in agricultural production could reduce the demand for mineral P fertilizers. This study investigated the effectiveness of three sewage sludge ashes (SSA) produced by different thermal conversion technologies (two types of gasification and one thermal-chemical post-treatment) and by precipitation (struvite) through chemical extractions and a greenhouse experiment with maize.

Methods: P solubility in water and organic acids, and a sequential extraction were performed to characterize plant-available P and the distribution of P in different fractions in the recycled products. Heavy metal concentrations in the recycled products were also determined. Additionally, the fertilizer P use efficiency was determined through a greenhouse experiment with young maize, where recycled products were pre-incubated with two different substrates for 0, 22, and 56 days before sowing.

Results: Two gasified SSAs (SSA1 and SSA2) exceeded the maximum concentration of Ni and Pb according to the EU fertilizing product regulation, while post-treated SSA3 only exceeded the limit of Cu and Zn. The highest P use efficiency was found in struvite, followed by SSA3 in both substrates, which was similar to readily available mono-calcium phosphate. Increasing the pre-incubation time of recycled products with the substrate had a negative impact on their P use efficiency. The P solubility of recycled products poorly predicted their effectiveness as fertilizer. Sequential extraction showed large shares of recalcitrant P fractions in SSA3 and struvite, which contradicted the positive effects on maize growth in the greenhouse experiments. Calcium-acetate-lactate and Olsen extractions of fertilized soil correlated well with plant P contents.

Conclusions: Struvite and the post-treated SSA showed high potential as P fertilizers. Their application at sowing may be recommended when incorporated into the soil. Novel methods to chemically characterize recycled products or soil-fertilizer mixtures are required to predict the P fertilizer efficiency.

1. Introduction

Phosphorus (P) is an essential element in various biological processes, and it is one of the macronutrients indispensable for agricultural crop production. It is mostly derived from phosphate rock, a non-renewable raw material for commercial mineral P fertilizer production. The world reserves of phosphate rock are mainly located in Morocco and Western Sahara, China, and Algeria (USGS, 2021). Solutions to alleviate the dependency on phosphate rock for agricultural purposes include increasing fertilizer efficiency, preventing P losses, and recycling P from waste streams (Cordell et al., 2009; van Dijk et al., 2016).

An investigation of P flows and balances in European Union countries showed that the biggest waste output of P was through municipal waste (691 Gg P), mainly ending up in wastewater treatment plants (Schoumans et al., 2015). The direct application of sewage sludge is the most straightforward method of returning P to primary production systems. However, it raises concerns about potentially depositing pollutants in agricultural soils and posing a threat to human health along with the food chain. Therefore, the European Commission restricted the use of sewage sludge, making it necessary to identify other pathways of returning P from wastewater streams. Also, legislative pressure toward the recycling of P from waste streams, such as the German new sewage sludge regulation launched in 2017 (Bundesministerium für Umwelt, 2017), calls for increased technological innovation and scientific research efforts. Possible solutions lie in the recovery of P from thermal oxidation or gasification of sludge and the recovery from the liquid phase before and after sludge dewatering.

Sewage sludge ash (SSA) is the by-product of mono-incineration for sludge disposal and energy production, whose P content can range between 2% and 13% depending on the nutrient content in the feedstock (*Fang* et al., 2018; *Schoumans* et al., 2015). The direct use of SSA as fertilizer is often questionable due to its low availability to plants (Severin et al., 2014; Wollmann et al., 2018). The crystalline form of P in SSA from the typical fluidized bed is mostly whitlockite ($Ca_3(PO_4)_2$), which is not immediately available to plants (Donatello, 2013). Post-treatment technologies have been developed to either retrieve P via the ash-leaching (Gorazda et al., 2017) or improve their P availabilities via the thermochemical process where the heavy metals are also removed in the final product (Herzel et al., 2016). In countries where the majority of sludge is discarded by combustion, like Germany (Eurostat, 2021), P recovery from wastewater via SSA can be realistic using existing equipment in wastewater treatment plants. Another recycled product that has drawn much attention is struvite ($NH_4MgPO_4 \cdot 6H_2O$), a precipitated salt from sludge. There are currently several struvite products available on the market which showed at least the same P fertilizer effect as single superphosphate (Muys et al., 2021). However, the maximum P recovery efficiency of struvite precipitation from sewage sludge covers a wide range from 67 to 99 % depending on the cations present in the sludge (C. Meyer et al., 2019; Muys et al., 2021). Therefore, it is challenging to achieve sufficient P recycling from sewage sludge by struvite precipitation. It is worth mentioning that precipitation as struvite-containing salt mixtures is also an option for the production of a high-value fertilizer from semi-liquid manure and biogas digestates (Lorick et al., 2020). For these materials, the P-recycling is usually above 90 %.

Recycled products from wastewater often contain a range of P species with different plant availability, which makes them different from phosphate rock-derived fertilizers (Nanzer et al., 2014; C. Vogel et al., 2018). It is difficult to easily assess the availability of recycled products from wastewater by extractive and analytical methods since indicators that are used to represent their P availability to plants can lead to quite different results even between the same type of products (Kratz et al., 2019). P solubility in neutral ammonium citrate was found as a better characterization of mid to long-term P availability of recycled fertilizers than that in the water (Kratz et al., 2010). Nanzer et al. (2019) applied an ion sink approach to predict plant-available P fractions by identifying three functional P pools in SSA, while Mackay et al. (2017) found diffusive gradients in thin films analysis correlated the most closely to the availability of SSAs. As many of the recycled products are not considered readily available fertilizers, the time when incorporated with soil may have an impact on their availability. Yet the effectiveness of recycled products as P fertilizer under varying incubation time is still unclear.

In this study, P pools of four recycled products, representing the full range from untreated and treated ashes to a precipitated salt were examined and their availability to young maize under three incubation time was investigated. It is hypothesized that the effectiveness of recycled products from different recycling processes varies and is influenced by the incorporated time with soil by comparing their P use efficiency in a greenhouse experiment.

2. Material and methods

2.1 Recycled products and analysis

Four products recycled from sewage sludge were tested. Two untreated ashes from the gasification of dry sludge (SSA1 and SSA2) were provided by Kopf Syngas GmbH (Hartmann et al., 2020). A Sodium-treated sewage sludge ash (SSA3) similar to rhenania phosphates (Messerschmitt, 1922) from the ASH DEC © process was provided by Outotec (Hermann & Schaaf, 2019). The ASH DEC © process introduces Na-containing alkaline compounds to form citrate-soluble $CaNaPO_4$ (Hermann & Schaaf, 2019).

The fourth fertilizer was a $MgNH_4PO_4 \cdot 6H_2O$ (struvite)-dominated precipitation product from digested sludge obtained through the "Stuttgart process" (C. Meyer et al., 2019).

The recycled products were oven-dried and ground (granule size < 0.5 mm ø) for further analysis. The concentration of P and other elements of interest in recycled products were determined after aqua regia digestion (VDLUFA, 2011b), and measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) (P) and inductively coupled plasma-mass spectrometry (ICP-MS) (Fe, Mg, Al, Cu, Cr, Ni, Zn, Cd, Pb). The P pools in recycled products were analyzed by the sequential extraction method modified by Hedley et al. (1982). 0.5 g samples were sequentially extracted with 30 ml of each extractant: deionized water, 0.5 M sodium bicarbonate ($NaHCO_3$) with a pH of 8.5, 0.1 M sodium hydroxide (NaOH) and 1 M sulfuric acid (H_2SO_4). Samples were shaken at 180 rpm for 16 hours during each extraction and then P concentration in the supernatant was measured by ICP-OES. The residual P pool was calculated by subtracting the sum of extracted P from the total P. The analysis of P solubility in water and neutral ammonium citrate (NAC) and in 2% citric acid followed the method of VDLUFA (1995a, b). Abbreviations of tested products and their P solubility in water and organic acids are listed in Table 1.

Table 1: Abbreviation, main P component, total P and N concentration (data from Table S1), and P solubility in water (P_{H2O}), neutral ammonium citrate (P_{NAC}), and 2% citric acid ($P_{2\%\ CA}$) of recycled products

Recycled product	**Abbreviation**	**Main P Component**	**Total P**	**P_{H2O}**	**P_{NAC}**	**$P_{2\%\ CA}$**	**N**
			(mg g^{-1}) DM	(% of total P)			(%)
Ash product	SSA1	$(Ca,Mg)_3(PO_4)_2$ $Ca_3Mg_3(PO_4)_2$	52	0.3	47.1	38.5	<0.1
	SSA2	$Ca_3Mg_3(PO_4)_2$	80	0.4	51.7	35.7	<0.1
	SSA3	$CaNaPO_4$	70	1.9	65.1	62.9	<0.1
Precipitation product	STR	$MgNH_4PO_4 \cdot 6H_2O$	120	4.1	62.1	92.8	4.8

2.2 Greenhouse experiment

Two substrates were used for the greenhouse experiment. Substrate 1 was a 1:1 mixture of silica sand and loamy clay topsoil (pH_{CaCl2}: 5.6, P_{CAL}: 40 mg kg^{-1}, P_{Olsen}: 16 mg kg^{-1}, carbonates: 1%). Substrate 2 was a 3:1 mixture of silica sand and a silty loam subsoil (loess, pH_{CaCl2}: 7.6, P_{CAL}: 40 mg kg^{-1}, P_{Olsen}: 2 mg kg^{-1}, carbonates: 5.6%). The silica sand was used to further decrease the soil P concentration in the final substrate.

The four recycled products (SSA1, SSA2, SSA3, STR), a positive control with mono-calcium phosphate (MCP) and a negative P control (CON) were included in the greenhouse experiment as fertilizer treatments with three replicates each. On the 11th of June in 2018, two substrates were homogenously mixed with each fertilizer treatment (100 mg P kg^{-1} soil) respectively and filled into standard Mitscherlich pots (4.7 kg dry substrate pot^{-1}). Pots were watered to 60% of substrate water holding capacity and kept at this moisture content for an incubation period of 56 days in the greenhouse. On the 16th of July, another batch of pots was prepared in the same way and incubated for 22 days. During the incubation of two batches of pots, the average temperature in the greenhouse was 23.6 °C in June and 26.5 °C in July. On the 8th of August, the third batch of pots was prepared without any incubation, and three maize seeds (var. Sulano) were sown in each pot of three batches. Seedlings were reduced to one per pot after emergence. Nutrient solutions, except for P, were applied after sowing to ensure the appropriate fertility of substrate for plant growth. Applied nutrients were: 120 mg N kg^{-1} as NH_4NO_3, 150 mg K kg^{-1} as K_2SO_4, and 50 mg Mg kg^{-1} as $MgSO_4$. Nitrogen application was reduced for STR treatment by subtracting the N content applied with STR. As substrate 2 only consists of pure loess and sand, micronutrients were applied as well: 2.6 mg Zn kg^{-1} as $ZnSO_4$, 1 mg Cu kg^{-1} as $CuSO_4$, 2.2 mg Mn kg^{-1} as $MnSO_4 \cdot 2H_2O$, 0.54 mg Mo kg^{-1} as $Na_2MoO_4 \cdot 2H_2O$, 0.86 mg B kg^{-1} as H_3BO_3.

After 40 days of growth, above-ground biomass and root were harvested, carefully washed with deionized water, and dried at 60 °C.

2.3 Sample preparation and analysis

Soil samples from each pot were taken on the day of sowing. Samples were air-dried and passed through a 2 mm mesh sieve. Two different methods were conducted to characterize soil plant-available P: calcium-acetate-lactate (CAL) extraction method and Olsen extraction method (Olsen, 1954; VDLUFA, 2012). For the CAL method, 5 g of air-dried soil was extracted in 100 mL CAL extraction solution (0.05 M calcium acetate, 0.05 M calcium lactate, and 0.3 M acetic acid, adjusted to pH 4.1) and shaken for 90 minutes. 3 g of CAL-washed active charcoal was added before shaking to prevent the disturbance from the color of humus in the soil. The extracts were filtrated with 150 mm MN 619 G filter paper and measured using ammonium vanadate/molybdate as a coloring agent and determined by photometry at 540 nm wavelength. For the Olsen method, 5 g of air-dried soil was extracted in 0.5 M $NaHCO_3$ with a pH of 8.5 and shaken for one hour. The extracts were filtrated with P-free filter paper and the extracted P concentration was determined using ICP-OES.

Plant samples were ground and digested in aqua regia solution (VDLUFA, 2011a). P concentration was determined by photometry using vanadate/molybdate as a coloring agent. Shoot P content was calculated as the product of plant P concentration and shoot biomass dry matter.

The calculation of P use efficiency (PUE) is calculated as the ratio between apparent P uptake from fertilizer treatment and fertilized P (235 mg P pot^{-1} for substrate 1 and 353 mg P pot^{-1} for substrate 2):

$$PUE\ (\%) = \frac{\text{P content (treatment)} - \text{P content (Zero P control)}}{\text{Fertilized P}} \times 100$$

2.4 Data analysis

The greenhouse experiment was managed in a completely randomized design. Statistical analysis was performed using the R environment for statistical computing (*R Core Team*, 2019). A two-way analysis of variance (ANOVA) model with fertilizer treatment (df = 5) and incubation time (df = 2) as factors were used to test the effect of each factor and their interaction on shoot biomass, root biomass, shoot P concentration and shoot P content of maize. When a significant difference was found, multiple comparisons between fertilizer treatments and between incubation time were conducted using Tukey test. The relation between CAL-P/Olsen-P determination and plant P content under different incubation time periods was tested through Pearson correlation.

3. Results

3.1 Properties of the recycled products

The total P content of recycled products varied between 5.2% (SSA1) to 12% (STR). Three SSAs generally had lower P content than STR and nearly no nitrogen. STR contained almost 9 times higher Mg than SSAs (Table 2). SSAs had much higher Fe and Al concentrations than STR. Among the three SSAs, SSA3 contained 2-3 times less Fe than SSA1 and SSA2. For heavy metals that are potentially toxic to plants and the environment, STR had lower concentrations than the three SSAs, which were also below the maximum value designated by the EU fertilizer regulation and the German Fertilizer Ordinance. However, the concentration of one or more selected heavy metals in the three SSAs exceeded the maximum value in the two regulations, which restricts their use as P fertilizer.

Table 2. Total concentration of magnesium (Mg), iron (Fe), aluminum (Al), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in the dry matter of the recycled products and maximum concentration of Cd, Cu, Ni, Pb, Zn in fertilizers according to the EU regulation and to the German Fertilizer Ordinance (*Düngemittelverordnung*, 2012; *European Council*, 2019). For recycled product abbreviations see Table 1.

Recycled product	Mg	Fe	Al	Cd		Cr	Cu	Ni	Pb	Zn
		(g kg^{-1})		(mg kg^{-1} P_2O_5)	(mg kg^{-1})			(mg kg^{-1})		
SSA1	12.7	135.7	47.7	10.8	1.3	222.6	1237	115.9	71.1	2845
SSA2	10.7	172.0	24.4	4.4	0.8	106.7	535	94.4	160.2	2664
SSA3	13.5	59.3	51.2	4.4	0.7	87.1	624	58.6	38.0	1745
STR	91.8	29.9	0.2	1.1	0.3	4.1	5	1.5	5.2	4.4
EU regulation	-	-	-	60.0 [2]	3.0 [3]	-	600	100	120	1500
German Fertilizer Ordinance	-	-	-	50.0 [2]	1.5 [3]	-	-	80	150	-

All recycled products showed low P solubility in water, ranging from 0.3% (SSA1) to 4.1% (STR) of total P (Table 1). In the two untreated SSAs (SSA1 and SSA2), around 50% of P was soluble in neutral ammonium citrate (NAC) while 30-40% of P was soluble in 2% citric acid. SSA3 contained more than 60% of P soluble in NAC and citric acid. STR also contained more than 60% of P soluble in NAC and more than 90% of P soluble in citric acid. The distribution of P pools characterized by sequential extraction also varied between tested materials (Figure 1). Between 70-78% of P in the SSAs were H_2SO_4-P, while readily soluble water- and $NaHCO_3$-P only comprised less than 3%. STR contained a larger share in water- and $NaHCO_3$-P (7%) and less H_2SO_4-P than the other products. The highest NaOH-P fraction was found in STR (39%), followed by SSA2 (14%), SSA1 (6%), and SSA3 (2%).

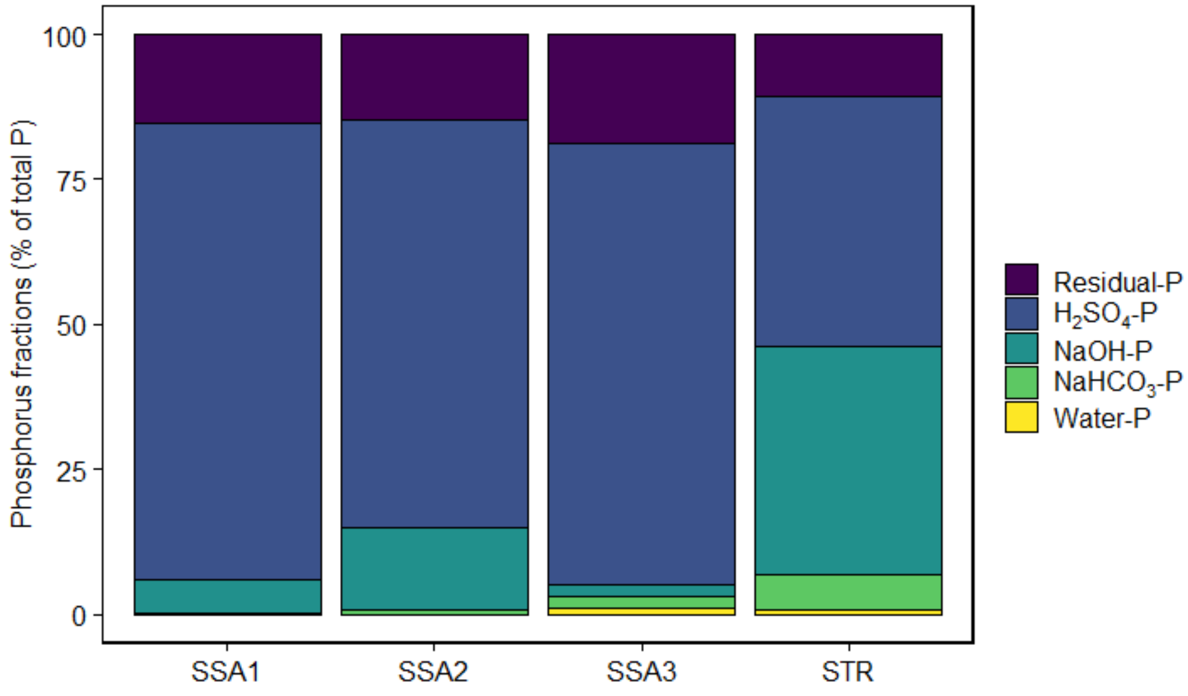


Figure 1. Phosphorus fractions (% of total P) by sequential extraction of water-, $NaHCO_3$-, NaOH-, H_2SO_4-, and residual-P in SSA1, SSA2, SSA3 and STR.

3.2 Greenhouse experiment

Substrate properties after mixing with the recycled products varied among the fertilizer treatments (Table 3). In substrate 1, the addition of MCP and the three SSAs decreased the substrate pH, while STR merely changed the substrate pH. CAL-P and Olsen-P in the MCP and STR treatments were more than two-fold higher than it in CON. SSA3 application doubled the CAL-P compared to CON but not the Olsen-P. SSA1 increased 35% of CAL-P in the substrate but not the Olsen-P. SSA2 barely changed the substrate CAL-P or the Olsen-P. In substrate 2, the extent of pH change by the application of recycled products was small. The change of CAL-P by the fertilizer treatments were similar to it in substrate 1. MCP, SSA3 and STR substantially increased the substrate Olsen-P.

Maize differed in growth response to the fertilizer treatments and incubation times in the two substrates. In substrate1, the interaction of fertilizer treatment and incubation time had an effect only on the shoot P content (Table S2). In general, SSA3 and STR resulted in similar shoot biomass, root biomass and shoot P content as readily available fertilizer MCP in two substrates respectively (Figure 2). They promoted shoot biomass and P content 3 folds more than SSA1 and SSA2. SSA1 and SSA2 failed to significantly improve the growth of maize shoot and root compared to the negative P control (CON). Within the same fertilizer treatment, pre-incubation had a negative impact on the maize growth and P uptake, where the highest value was found without incubation (Incubation time 0).

Table 3. pH_{CaCl2}, CAL-P and Olsen-P of Substrate 1 and Substrate 2 without P addition (CON) and right after the application of MCP, SSA1, SSA2, SSA3 and STR (mean value ± standard deviation). For abbreviations see table 1.

Treatment	Substrate 1			Substrate 2		
	pH_{CaCl2}	CAL-P (mg kg^{-1})	Olsen-P (mg kg^{-1})	pH_{CaCl2}	CAL-P (mg kg^{-1})	Olsen-P (mg kg^{-1})
CON	5.6 ± 0.1	42.4 ± 3.2	21.2 ± 0.4	7.4 ± 0.08	42.9 ± 1.9	2.2 ± 0.1
MCP	5.1 ±0.1	90.3 ± 10.6	62.6 ± 11.7	7.3 ± 0.05	92.2 ± 4.6	45.1 ± 6.4
SSA1	5.1 ± 0.03	57.0 ± 6.7	20.6 ± 1.7	7.4 ± 0.1	54.1 ± 1.7	-
SSA2	5.2 ± 0.1	44.7 ± 3.3	19.9 ± 2.4	7.5 ± 0.03	49.7 ± 4.6	3.3 ± 0.2
SSA3	5.2 ± 0.05	84.9 ± 8.0	25.3 ± 0.7	7.6 ± 0.05	103.8 ± 2.1	12.5 ± 1.1
STR	5.5 ± 0.2	95.3 ± 2.8	65.4 ± 2.4	7.2 ± 0.03	100.1 ± 12.0	64.8 ±16.2

However, in substrate 2, all measured plant growth indicators were affected by the interaction between two factors. Similar to it in substrate 1, SSA3 and STR resulted in similar shoot biomass, root biomass and shoot P content as MCP, while the highest value was found at incubation time 0 within the same fertilizer treatment. Shoot biomass and P content of SSA3 and STR were 10 folds greater than that of SSA1, SSA2 and Zero-P control. Root growth under SSA1 and SSA2 application were also significantly restricted compared to the other fertilizer treatments.

P use efficiency (PUE) of four recycled products and MCP after incubation times of 0, 22 and 56 days are shown in Table 4. In substrate 1, the maximum PUEs of all fertilizer treatments were obtained without pre-incubation, which decreased with increasing incubation time period. SSA1 and SSA2 only had a maximum PUE of 2% and 3%. The maximum PUE of SSA3 and STR were 8% and 11% respectively, where the latter was the same as that of MCP. In substrate 2, SSA1 and SSA2 almost had no PUE after all incubation times, while SSA3 had a maximum PUE of 4% under 0 day of incubation. STR had a maximum PUE of 11% after 22 days of incubation, which was 2 times higher than MCP.

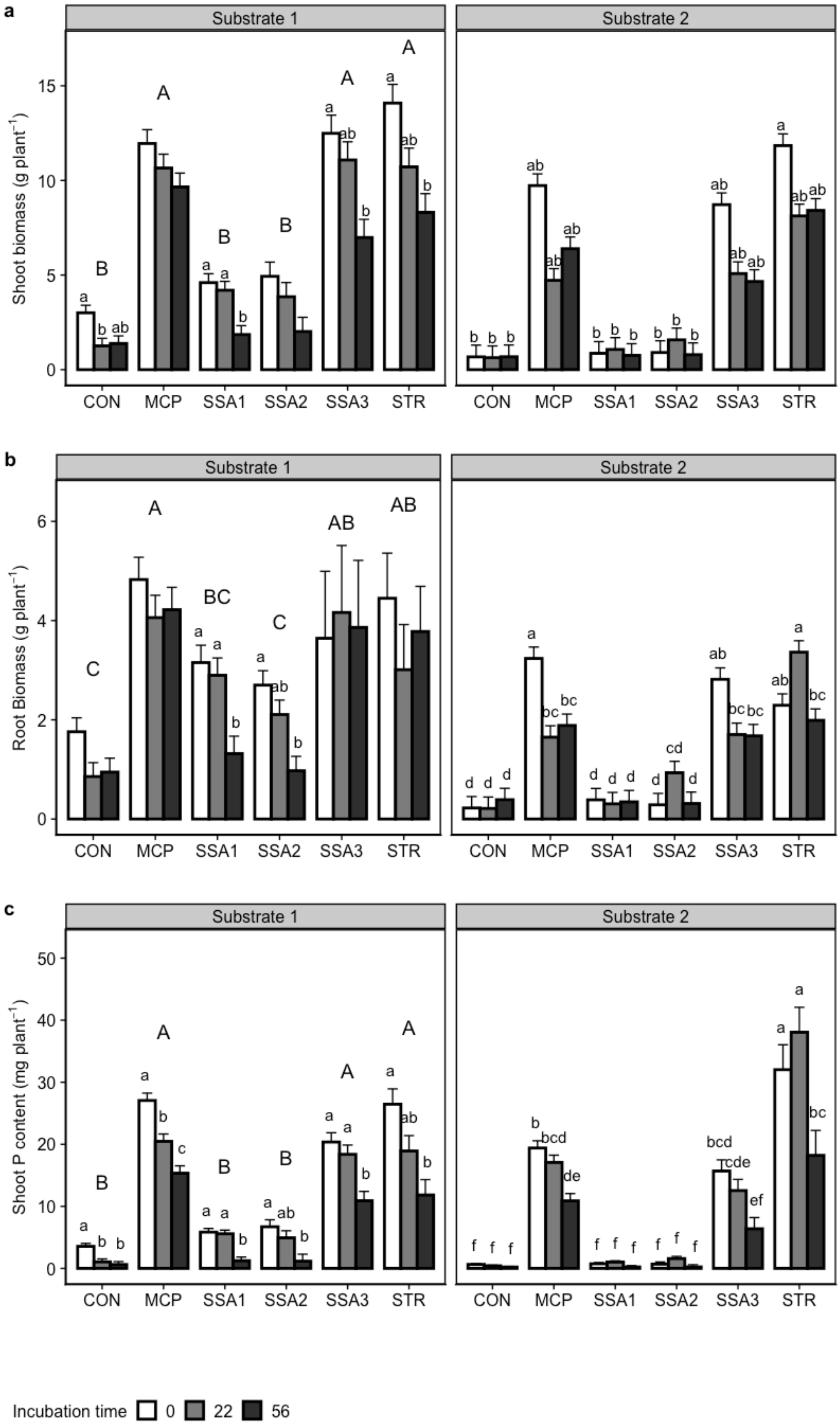
Table 4. P use efficiency (%) of recycled products and MCP after incubation times of 0 ,22, 56 days. For Abbreviations see table 1.

	Substrate 1			**Substrate 2**		
Incubation time period	0	22	56	0	22	56
SSA1	2 a	2 a	0.3 b	0.03 ab	0.1a	- 0.1 b
SSA2	3 a	2 ab	0.2 b	0.02 b	0.3 a	-0.1 b
SSA3	8 a	8 a	4 b	4 a	3 ab	2 b
STR	11 a	8 ab	5 b	9 a	11 a	5 b
MCP	11 a	8 b	6 c	5 a	5 a	3 b

The correlation of plant P content and soil P extraction varied between the three incubation times (Table 5). In substrate 1, CAL-P correlated well with the plant P content, where the longer the substrate was incubated, the weaker the correlation was found. Olsen-P had the strongest correlation with plant P content at 56 days of incubation, which was close to that at 0 days of incubation. In substrate 2, CAL-P significantly correlated with plant P content after all incubation times, where the strongest correlation was found without pre-incubation. Olsen-P had the strongest correlation without pre-incubation. After 22 days of incubation, the correlation was not significant.

Table 5. Spearman correlation (N = 12) coefficient of soil CAL-P and Olsen-P (fertilized with recycled products SSA1, SSA2, SSA3 and STR, see table1) with plant P content at 0, 22 and 56 days of incubation time. *** = $p \leq 0.001$, ** = $p \leq 0.01$, * = $p \leq 0.1$, ns = not significant.

	Plant P content (mg pot^{-1})					
	Substrate 1			Substrate 2		
Incubation time period	0 day	22 days	56 days	0 day	22 days	56 days
CAL-P (mg pot^{-1})	0.8**	0.73**	0.67*	0.77**	0.57*	0.70*
Olsen-P (mg pot^{-1})	0.85***	0.73**	0.89***	0.9***	0.31 ns	0.79**


a
Substrate 1
Substrate 2
Shoot biomass (g plant^{-1})
0
5
10
15
B
A
B
B
A
A
a
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ab
a
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ab
CON
MCP
SSA1
SSA2
SSA3
STR
b
Substrate 1
Substrate 2
Root Biomass (g plant^{-1})
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2
4
6
C
A
BC
C
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AB
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ab
a
bc
CON
MCP
SSA1
SSA2
SSA3
STR
c
Substrate 1
Substrate 2
Shoot P content (mg plant^{-1})
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40
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bc
CON
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SSA1
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SSA3
STR
Incubation time
☐ 0
▨ 22
■ 56

Figure 2. Shoot biomass (a), root biomass (b) and shoot P content (c) of maize under fertilizer treatments and incubation time periods of 0, 22, 56 days.

4. Discussion

4.1 Contaminants in the recycled fertilizers

The nutrient and heavy metal concentrations varied between analyzed recycled products, which largely depended on their feedstock and production process. For gasified SSA1 and SSA2, high concentrations of Ni, Pb, Cu, and Zn which exceeded the corresponding maximum value in the EU and German fertilizer regulation may originate from the industrial sludge in their feedstock. In a German SSA survey, about 59% of SSA derived from industrial processes or from a mixture of municipal/industrial sludge, which resulted in a significant accumulation of heavy metals (Krüger & Adam, 2015). Krüger et al. (2014) found a generally lower Cd and U concentration but higher Pb and Hg concentration in SSA than in phosphate rock. Separation of industrial and municipal sludge before incineration might reduce the heavy metal accumulation and elevate the P concentration in SSA if considering that most P from human excreta and P-containing household detergents end up in municipal wastewater. To avoid heavy metal contamination, several acid-leaching methods were encouraged to extract P in SSA for the production of P-rich leachate or P fertilizer (Fang et al., 2018; Gorazda et al., 2017; Ottosen et al., 2013). The thermochemical post-treatment in the production of SSA3 was also designed to remove heavy metals in a reducing atmosphere over 950°C (Hermann & Schaaf, 2019). Our results showed that the concentration of heavy metals without a nutritional value (Cd, Ni, Pb) in SSA3 lay within the EU and German limits for fertilizer. However, because the sludge used to produce SSA1-3 was different, the low heavy metal concentration in SSA3 was hardly evidence of effective heavy metal removal. STR contained much lower concentrations of heavy metals than the three SSAs and a considerable amount of beneficial nutrient Mg, suggesting the advantage of precipitation products in the exclusion of heavy metal from sludge.

4.2 P availability of recycled fertilizers to plant

Results from the greenhouse experiment showed poor P availability of the two untreated SSAs (SSA1 and SSA2) to young maize in both substrates. The main P component in two SSAs (Table 1), whitlockite, was barely available to plant and therefore the majority of P in two SSAs was H_2SO_4-P (Figure1). Severin et al. (2014) also found a low P availability of untreated SSA in maize in an acidic substrate with similar P doses per pot. The composition and quality of SSAs as P fertilizers largely depend on the combustion process. Within the same thermal process, different designs and conditions result in ashes with different qualities (Thomsen et al., 2017). Processing the same sludge with different combustion techniques, dried and incinerated sludge increased wheat growth while gasified and pyrolyzed sewage sludge failed (J. E. Mackay et al., 2017). The P availability of SSAs can also vary when fertilized in different soils. Both SSA1 and SSA2 showed higher PUEs in substrate 1 than in substrate 2. Due to the dissimilarity of the two substrates, it is hard to explain why SSA1 and SSA2 behaved differently. However, several studies showed that soil pH may influence the P availability of SSAs. Cabeza et al. (2011) found a higher efficiency of a calcium phosphate-dominated recycled fertilizer in a strongly acidic substrate (pH 4.7) than in a moderately acidic substrate (pH 6.6). Vogel et al. (2018) also demonstrated a greater yield of maize in an acidic soil (pH 4.9) than in a nearly neutral soil after application of a SSA that contained P mainly as Mg-phosphate and chlorapatite ($Ca_5(PO_4)_3Cl$). An additional treatment with mineral acid may mobilize plant-available P compared to the untreated ash to some extent, which is similar to the enhancement of P availability in phosphate rock (M. Hedley & McLaughlin, 2015). A pot experiment with young maize showed the potential of partly replacing rock phosphate with untreated SSA when producing superphosphate as a P fertilizer (Hartmann et al., 2020). Nevertheless, the contaminants in SSA should also be considered when bringing it to practical use.

SSA3 resulted in similar maize growth and P uptake as MCP in both substrates after all incubation times. The production of SSA3, the Ash Dec© process, introduces Na-containing alkaline compounds to form citrate-soluble $CaNaPO_4$ (Hermann & Schaaf, 2019). However, this high PUE of the same SSA3 was not found in a previous field experiment (Wollmann & Möller, 2018). Despite other factors (fertilizer application method, soil available P status) influencing the fertilizer efficiency of SSA3, more studies are needed at the field scale to evaluate this contradiction.

STR was as effective as readily available fertilizer MCP in both substrates in promoting young maize growth and P uptake. Its highest P use efficiency (PUE) was the same as MCP in substrate 1. In substrate 2, STR achieved a significantly higher shoot P content and greater PUEs than MCP under 0 and 22 days of incubation, which indicated a greater P availability than MCP in the calcareous low-P substrate. Vogel et al. (2018) also found a slightly higher yield of maize by struvite application than by triple superphosphate application in acidic and nearly neutral substrates. They attributed these results to the higher content of ammonium in struvite compared to other tested recycled fertilizers. *George* et al. (2016) drew the same conclusion based on a hydroponic experiment. Other studies also proposed a synergistic effect of Magnesium (Mg) in struvite (T. Vogel et al., 2015). However, this explanation is weak for our experiment where Mg was applied to all treatments. The PUE of STR without incubation was similar in substrate 1 (11%) and in substrate 2 (9%). Although the soil properties of the two substrates differed, previous studies suggested soil pH might influence the P availability of struvite. Usually, struvite shows its minimum solubility when pH is above 8 and it is reckoned that its dissolution increases under lower pH conditions (C. Meyer et al., 2019). A meta-analysis on the agricultural potential of struvite also showed the negative impact of increasing soil pH on the relative plant P uptake (Hertzberger et al., 2020). The granule size of struvite is also a crucial factor influencing its P availability in soils differing in pH. Degryse et al. (2017) found a faster dissolution of struvite in acidic soil than in alkaline soil and it was negatively affected by its granule size. In our study, finely ground struvite (< 0.5 mm) was mixed into the substrate, which may have reduced the effect of soil pH on struvite dissolution. Under field conditions, where the fertilizer is often applied in granule forms, struvite has shown a slightly higher fertilizer efficiency than water-soluble P fertilizer in an acidic soil (T. Vogel, Nelles, et al., 2017). But whether it can have the same efficiency in fields with alkaline soil needs to be further investigated.

Struvite as P fertilizer has been intensively investigated, with the majority of it conducted under greenhouse conditions (Hertzberger et al., 2020). Following the revision of the EU fertilizing products regulation where struvite is listed under ‘precipitated salts and derivates’, it can be foreseen that struvite and struvite-like products from waste streams will contribute substantially to P recovery for agricultural propose.

The PUE of recycled products showed a descending trend with increasing incubation times in both substrates (Table 3). Significant decreases in PUE were found after 56 days of incubation compared to no pre-incubation. It was expected that pre-incubation of untreated SSAs (SSA1 and SSA2) would enhance PUE as found by Mackay et al. (2017). An increasing water extractability of P over time in SSA-amended soil was also found in the study of (Lemming et al., 2020), indicating a slow P-solubilizing reaction. It can be that the majority of soluble P in SSA1 and SSA2 dissolved right after being applied to soil, or the reaction product of P solution and soil particles restricted the further dissolution. Both possible reasons are related to the production process of SSA and soil characteristics, indicating the difficulty on conclude the general effectiveness of SSA as fertilizers. For SSA3 and STR, although they are also barely water-soluble, their high PUE may be due to their granule size and the application method. As Degryse et al. (2017) argued, when water-insoluble struvite was mixed homogenously with soil in powdered form, the enhanced contact surface between soil and fertilizer led to an increasing sorption of phosphate on the solid phase, which reduced the phosphate concentration in soil solution and further accelerated the struvite dissolution. If applied in granular form, the results may be different (Talboys et al., 2016).

4.3 Characterization methods on P availability of recycled fertilizers

The analysis of P solubility in different extractants is often applied to characterize the plant availability of a P-rich product, where water, neutral ammonium citrate (NAC), and 2% citric acid (CA) are widely used (Falk Øgaard & Brod, 2016; Möller et al., 2018). In this study, only small fractions of P in the four recycled products were water-soluble, which was consistence with the finding in other studies on recycled products from the wastewater (Krüger & Adam, 2017; Wollmann et al., 2018). However, the P solubility in water poorly predicted the P availability to plants according to the result of the greenhouse experiment. With less than 5% water-soluble P, STR resulted in significantly larger maize biomass and shoot P content than CON, which were in the same range as the water-soluble P fertilizer MCP. Alternative indicators other than the water solubility of P fertilizers are necessary for the characterization of the P availability (G. Meyer et al., 2018). NAC extraction was found to be well correlated with the agronomic performance of phosphate rock. Therefore, it was widely used to characterize phosphate rock-derived fertilizers (A. D. Mackay et al., 1984). Almost half of P in SSA1/SSA2 and more than 60% of P in SSA3 and STR were NAC-soluble P. In contrast, the greenhouse experiment showed a restrained growth of maize in both substrates after fertilization of SSA1 and SSA2, indicating a poor estimation of P availability by P_{NAC}. Kratz et al. (2019) found an overestimation of P_{NAC} of the P availability of recycled fertilizers because P species in recycled fertilizers that can largely dissolve in NAC are only available for the plant to a limited extent. The P solubility in 2% CA ($P_{2\%\,CA}$) characterized the P availability to maize in substrate 1 reasonably. However, in substrate 2, $P_{2\%\,CA}$ overestimated the P availability to the maize of SSA1 and SSA2, though it mimics the maize root exudates (Jones & Darrah, 1995). Common chemical extractions designated for phosphate rock-derived fertilizers may not be suitable to predict the P availability of recycled products, especially for thermal-converted products.

Sequential extraction was originally applied to characterize soil P fractions (M. J. Hedley et al., 1982). It was also adopted for recycled products for P fraction characterization to indirectly characterize the P availability (J. E. Mackay et al., 2017; G. Meyer et al., 2018; T.

Vogel, Kruse, et al., 2017). All tested recycled products had low readily available P (water- and $NaHCO_3$-P), although these P fractions were found to correlate best with plant P uptake or fertilizer efficiency in earlier investigations (J. E. Mackay et al., 2017; G. Meyer et al., 2018). NaOH-P represents P bound to Al- and Fe-components (M. J. Hedley et al., 1982), which may be present in large amounts in SSAs. The distribution of P fractions in SSA1 and SSA2 were consistent with other untreated Al/Fe-rich SSAs (Nanzer et al., 2014; T. Vogel, Kruse, et al., 2017), where NaOH and H_2SO_4 extracted most of the P. The considerable share of NaOH-P in STR compared to the other products may be due to the strongly alkaline environment (pH 13) of the extractant, where STR may show a high solubility (Harrison et al., 2011). H_2SO_4-P made up the largest share of total P in SSAs, which may be in relation to P bonding with Ca and Mg (T. Vogel, Kruse, et al., 2017). Thus, 76% of H_2SO_4-P in SSA3 are in accordance with rhenanite (Ca-Na-PO_4) as the main P-phase (Hermann & Schaaf, 2019). Nevertheless, the distribution of P fractions as characterized by sequential extraction was not consistent with the results of the greenhouse experiment, indicating a weak characterization of the P availability of recycled products. Novel methods such as ion sink assays or the diffusive gradients in thin films (DGT) might be more appropriate to predict the P availability of recycled products as fertilizers (Kratz et al., 2019; Nanzer et al., 2019).

Soil CAL and Olsen extraction correlated well with maize shoot P content in both substrates after all incubation times (Table 5). Franz et al. (2018) found plant P uptake correlated with Olsen-extracted P ($r = 0.3$) but not with CAL-extracted P in 50 different soils without fertilizer addition. In soils amended with dried and thermally converted sludge, Colwell-extracted P and DGT-P correlated best with the P uptake of ryegrass (J. E. Mackay et al., 2017). Although soil extractions of soil-fertilizer mixtures are not as rapid and easy as single-chemical extraction of fertilizers, it might be a suitable method to predict the P availability of recycled products.

5. Conclusion

In this study, three types of recycled fertilizers were evaluated for their P availability to young maize and the relationship between plant response and P availability characterization methods. Struvite and SSA3 showed great potential to supply P for crop cultivation, where struvite may even compete with the water-soluble fertilizer. Untreated SSAs (SSA1 and SSA2) with exceeding Ni and Pb concentrations ineffectively promoted the growth and P uptake of maize at the early stage. Chemical extractions of pure recycled products poorly characterized their effectiveness as P fertilizer, while CAL and Olsen extractions of soil-fertilizer mixtures correlated well with plant P content.

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Data Availability Statement

The data presented in this study are available in insert article and supplementary information

Supplementary information

Table S1. Additional information on struvite analysis. FM: fresh matter. DM: dry matter. Data provided by Landwirtschaftliche Untersuchungs- Und Forschungsanstalt Speyer.

		Method
Dry substance	60.7 % FM	DIN EN 12880:2001-02
pH-value	8.86	DIN EN 15933:201-11
Ash	43.7 % FM	DIN EN 12879:2001-02
Organic carbon	2.76 % DM	DIN ISO 10694:1996-08
Total nitrogen (N)	4.81 % FM	DIN EN 25663:1993-09
Ammonium-N	4.54 % FM	DIN 38406-5: 1983-10
Potassiumoxide (K_2O)	0.16 % FM	DIN EN 13346:2001-04
Calciumoxide (CaO)	7.8 % FM	VDLUFA MB Bd. II.2, 4.5.1:2008
Total sulphur	0.389 % FM	DIN EN 13346:2001-04

Table S2. Two-way ANOVA result of shoot biomass, root biomass and shoot P content for fertilizer treatments and incubation time periods in two substrates.

Substrate	Variable	Fertilizer treatments			Incubation time periods			Fertilizer treatment × Incubation time periods		
		df	F	*P*-value	df	F	*P*-value	df	F	*P*-value
1	Shoot biomass	5	90.9	< 0.001	2	30.6	< 0.001	10	1.7	0.119
	Root biomass	5	8.4	< 0.001	2	2.2	0.123	10	0.5	0.858
	Shoot P content	5	116.8	< 0.001	2	52.5	< 0.001	10	3.1	0.006
2	Shoot biomass	5	112.9	< 0.001	2	18.5	< 0.001	10	4.6	< 0.001
	Root biomass	5	67.3	< 0.001	2	5.8	0.006	10	6.1	< 0.001
	Shoot P content	5	249.1	< 0.001	2	39	< 0.001	10	10.1	< 0.001

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4. Chapter II

Producing superphosphate with sewage sludge ash: assessment of phosphorus availability and potential toxic element contamination

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Producing Superphosphate with Sewage Sludge Ash: Assessment of Phosphorus Availability and Potential Toxic Element Contamination

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Abstract: Recovering and recycling phosphorus (P) from sewage sludge ash (SSA) for the purpose of P fertilizer production contributes to reducing the input of mined phosphate-minerals and closing of the P cycle. However, direct use of SSA as fertilizer is often a questionable strategy due to its low nutrient use efficiency. In addition, the environmental risk potential of utilizing SSA in agriculture is still unclear, in particular potential toxic element (PTE) contamination. In this study, a mixture of SSA and rock phosphate was used at lab-scale superphosphate (SP) production. P availability of the final product and PTE contamination (Cd, Cr, Cu, Zn, Pb, Ni) in soil and crop was investigated through maize (*Zea mays* L.) cultivation. Results showed that the application of SP that was produced by 25% SSA replacement did not affect the growth, P uptake, and PTE content in aboveground maize compared to the application of SP produced without SSA replacement. However, significant inputs of SP with SSA replacement may decrease the solid-soil solution partitioning of Cu, Ni and Pb in the long-term. Separation of municipal/industrial sludge and PTE removal technology are necessary to be implemented prior to the use of SSA as a secondary raw material in P-fertilizer production.

Keywords: nutrient recycling; P availability; sewage sludge ash; potential toxic element

1. Introduction

Phosphate rock is the primary raw material for producing mineral phosphate fertilizers. Based on its economic importance and supply risk due to its non-substitutable and limited reserves around the world, it is regarded as one of the critical raw materials by the European Commission [1]. Additionally, it is recently identified to have high environmental hazard potential (EHP) concerning its raw material and energy demand [2]. Intrinsic potential toxic elements (PTEs) in phosphate rock also contribute to its high EHP as one of the indicators. In particular, heavy metals like Cadmium (Cd) and Uranium (U) become more bioavailable after the acidification process in the production of superphosphate (SP) or triple superphosphate (TSP) using phosphate rock. An evaluation of the phosphorus (P) fertilizer market in Germany determined that P fertilizers derived from phosphate rock may show Cd concentrations beyond the legal limits [3]. As natural P resources are decreasing, and the remaining resources show reduced quality, alternative P sources are needed to avoid a supply risk and the bioaccumulation of PTEs in humans through the food chain that involves phosphate rock-derived fertilizers and feed-additives.

In Europe, about 35% of total P loss from the consumption sector ends up in communal sewage sludge [4]. Since 2009, Germany has the largest share of annual municipal sewage sludge production in the EU with around 1.8 million tons, of which 60% was incinerated for disposal purposes [5]. The median P concentration of German sewage sludge ash (SSA) was 8%, which offers a great potential for an alternative P source for fertilizers [6]. However, the crystalline form of P in SSA from typical fluidized bed mono-combustion (800–900 °C) is usually a whitlockite-like calcium phosphate ($Ca_3(PO_4)_2$), which is not immediately plant-available [7]. Several processes have been developed to recover P from SSA, including acid leaching and various thermochemical methods [8,9]. An alternative way without a need for additional equipment is to substitute rock phosphate (RP) by SSA in the production of superphosphate (SP) [10]. The original production process of superphosphate is relatively simple, where finely grounded rock phosphate is acidulated with sulphuric or phosphoric acid [11]. It has raised the possibility of recycling P from SSA via existing equipment and technologies to produce P fertilizers.

A previous study found reduced growth of young maize plants when fertilized with SP that produced from a mixture contained more than 11% of SSA, which may be due to the low P availability of sulphuric acid-treated SSA [10]. To raise the share of SSA in SP while maintaining the maize biomass production, an increased amount of concentrated sulphuric acid (95%) related to the P concentration of SSA is required.

However, recycling P from waste streams in agricultural production could be hazardous to product quality and soil health due to the transfer of PTEs. Although SSA incinerated in Germany show considerably lower Cd and U concentrations than phosphate rock, there is an indication for higher lead (Pb) and mercury (Hg) concentrations [6]. Little is known about the accumulation of these PTEs in plants when fertilizing with SSA or SSA-based products. Therefore, the aim of this work was, firstly, to evaluate the P availability of SP produced from the mixture of SSA and RP and, secondly, to investigate PTE contamination in soil and plants. P use efficiency and PTE accumulation in plant and soil by the application of SP produced from SSA and RP were compared with SP produced from RP and with Struvite ($MgNH_4PO_4 \cdot 6H_2O$), a sludge-derived precipitated salt with a consistently high P availability [12]. We hypothesized that SP produced from SSA and RP will be as effective as traditional SP at increasing growth and nutrient uptake of maize without enhanced PTE contamination risk to plants and soil.

2. Materials and Methods

2.1. Superphosphate Preparation and Analysis

The rock phosphate (RP) used in the preparation was predominantly fluor- and hydroxyapatite (Origin: Israel) with a P concentration of 11.8%. The sewage sludge ash (SSA) used for the replacement of RP was produced from the gasification process SÜLZLE KOPF Syngas® and had a P concentration of 8.9% [13]. Qualitative analysis of the mineral structure of the ash was determined through X-ray diffraction (XRD, Siemens D5000), where $Ca_3Mg_3(PO_4)_2$ comprised most of the crystalline P compounds [10]. Iron phosphate, hematite, and magnetite may also be present depending on the iron content in the sludge [13]. Two superphosphates (SPs) (SP-0 and SP-25) were produced on a laboratory scale by the method described by [10] with some modifications.

SP-0 was produced solely of RP. SP-25 was produced from a mixture containing 25% SSA and 75% RP. All the raw materials in the two SPs were finely ground using a rotating disc mill before the acid digestion with sulphuric acid (95%) (0.4 mL g^{-1} RP and 0.5 mL g^{-1} SSA). The resulting SPs were then dried at 105 °C and ground into fine particles (granule size < 0.5 mm ø).

Total P and PTE concentration (Cd, Cr, Cu, Ni, Pb, Zn) in the tested fertilizers were determined through aqua regia digestion [14] and measured by inductively coupled plasma-mass spectrometry (ICP-MS) (Cd, Cr, Cu, Ni, Pb, Zn) and inductively coupled plasma-optical emission spectrometry (ICP-OES) (P). Since the tested SSA was produced from sludge using an iron compound as a precipitating agent, and the main crystalline P compound of Struvite (STR) is $MgNH_4PO_4 \cdot 6H_2O$, determination of Fe and Mg concentrations in the fertilizers were also included and measured by ICP-OES.

Extraction of P in the fertilizers with water and neutral ammonium citrate (NAC) followed the method of [15]. P extraction with 2% citric acid followed the method of [16]. All extracted P were determined by ICP-OES. The extraction results were calculated as the ratio of extracted P concentration and total P concentration.

2.2. Greenhouse Experiment

Besides the two SPs, the treatments included a precipitated phosphate salt from sewage sludge Struvite ($MgNH_4PO_4 \cdot 6H_2O$) [17], RP, the SSA used in SP preparation and a zero P control (Control) (Table 1). In total, there were six fertilizer treatments with four replicates each.

Table 1. Fertilizer treatments and their abbreviations, production processes, and mean concentrations of phosphorus (P), nitrogen (N), magnesium (Mg), and iron to P ratios.

Treatment	Abbreviation	Process	P	N	Mg	Fe/P
				$mg\ g^{-1}$		Molar Ratio
Sewage sludge ash	SSA	Gasification	89	<1	10	0.53
Rock phosphate	RP	Mining	118	<1	40	0.07
SP solely from RP	SP-0	RP digested with 95% H_2SO_4	73	<1	10	0.12
SP from 75% RP + 25% SSA	SP-25	75% RP and 25% SSA digested with 95% H_2SO_4	61	<1	9	0.34
Struvite	STR	Enforced P dissolution	120	52	100	0.04
No P fertilizer addition	CON	-	-	-	-	-

The experiment was conducted in a greenhouse from 21 May to 31 July 2019. The average air temperature during the plant growth period was 30.6 °C at day and 20.2 °C at night. A low-P loamy clay soil (pH_{CaCl2} 5.2, P_{CAL} 10 mg kg^{-1}) was mixed with 50% quartz sand to even further reduce its soil P level. The substrate was fertilized on dry matter basis with 120 mg P kg^{-1} using the different fertilizers (treatments), 120 mg N kg^{-1} as $Ca(NO_3)_2$ solution, and 150 mg K kg^{-1} as K_2SO_4 solution. All nutrients were mixed homogenously into the substrate.

5.5 kg of the prepared substrate was filled into a standard Mitscherlich-pot and brought to 65% of maximum water holding capacity. Three maize seeds (*Zea mays* var. Ricardinio) were placed 5 cm below the substrate surface and reduced to one plant per pot after emergence.

After ten weeks of growth (at silking stage), aboveground biomass was harvested and dried at 60 °C.

2.3. Plant P Content and P Use Efficiency

Plant dry matter was ground and digested according to the established wet-chemical extraction method [14]. Plant P concentration was determined using vanadate/molybdate as a coloring agent and measured by the spectrophotometer at 436 nm wavelength. Plant element concentrations were analyzed by ICP-OES (Fe, Mg) and ICP-MS (Cd, Cr, Cu, Ni, Pb, Zn) after aqua regia digestion. Plant P content was calculated as the product of plant P concentration and aboveground biomass dry weight.

The P use efficiency (%) of a fertilizer treatment was calculated as the difference of plant P content between the treatment and the No-P control divided by quantity of P applied with the fertilizer, which was 660 mg P per maize plant (Equation (1)):

$$\text{PUE}\ (\%) = \frac{\text{Plant P content (treatment)} - \text{Plant P content (control)}}{\text{mg P plant}^{-1}} \times 100\% \quad (1)$$

2.4. Soil Sampling and Analysis

Soil was sampled directly after fertilization (at sowing) and at harvest for the analysis of plant-available P and PTEs concentration. Samples were air-dried and passed through a 2 mm mesh sieve. Soil plant-available P was characterized by Calcium-Acetate-Lactate (CAL) extraction according to the established method [18]. Soil bioavailable Mg, Cu, and Zn was characterized through Calciumchlorid/DTPA (CAT) extraction [19]. The broadly applied EDTA extraction was used to characterize soil bioavailable Cd, Cr, Cu, Fe, Ni, Pb, Zn [20]. After the extraction, the determination of each element was performed by flame atomic absorption spectroscopy (F-AAS).

2.5. Statistical Analysis

Statistical analysis was performed using the R environment for statistical computing and graphical presentation [21]. After verifying the homogeneity of variance, one-way analysis of variance (ANOVA) was conducted to test the effect of the fertilizer treatment. When a significant effect was found, multiple comparisons of treatments were performed using Tukey's Honestly Significant Difference test.

3. Results

3.1. Phosphorus and PTE Content in Fertilizers

The P concentrations in both superphosphates (SP) were diluted by sulphuric acid. The 25% of rock phosphate (RP) replacement by sewage sludge ash (SSA) in SP-25 decreased its P concentration compared to SP-0 (no RP replacement). SP-25 had a similar Mg concentration as SP-0, but a larger Fe/P ratio (Table 1). The PTE mass concentrations in the tested P fertilizers were shown in Table 2. The maximum limits of PTE concentrations in inorganic fertilizers according to the European Union (EU) and German Fertilizer Ordinance were also listed [22,23]. RP contained the highest Cd concentration (2.0 mg kg^{-1}) among the tested fertilizers. SSA had the highest concentration of Cr, Cu, Ni, Pb, and Zn among the tested fertilizers and was the only fertilizer that exceeded the maximum concentration of Cu, Pb, Zn (EU regulation), and Ni (German Fertilizer Ordinance). The 25% replacement of RP by SSA in SP-25 resulted in significantly higher Cu, Pb, and Zn concentrations than in SP-0. However, Cd and Cr concentrations in SP-25 were less than the one in SP-0. The precipitated salt Struvite had the lowest concentration of all the listed PTEs.

Calculated mean inputs of the PTEs per kg P from the tested fertilizers were shown in Table 3. The RP replacement by 25% SSA in SP-25 production considerably increased Ni, Cu, Pb, and Zn input per kg P compared to SP-0.

The tested fertilizers showed great variations in P extracted with water, 2% citric acid and neutral ammonium citrate (NAC) relative to total P (Figure 1). For SP-0 and SP-25, water extracted more than half of their total P and organic acids extracted more than 75%. Struvite-P was almost fully extractable in citric acid but only a little of it was water-extractable. P in RP and SSA were not extractable in water, while SSA had higher P fractions that were extractable in organic acids than RP.

3.2. Bioavailability of P and PTEs in Fertilized Soil

Soil plant-available P characterized by CAL extraction at sowing varied under different fertilizer treatments (Figure 2). At sowing, STR had the highest value (44.6 mg kg^{-1}), followed by SP-25 (34 mg kg^{-1}) and SP-0 (27.1 mg kg^{-1}). At harvest, soil plant-available P in STR, SP-25, and SP-0 treatments remained in the P class B (low), indicating elevated soil plant-available P pools after plant removal. In contrast, P input from SSA and RP did not contribute to plant-available P in soil as characterized by CAL extraction in class A (very low) both at sowing and at harvest.

Table 2. Total concentrations of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) in dry matter (mg kg^{-1}) (unless otherwise noted) of the tested fertilizers and designated maximum concentrations of above-mentioned element in fertilizers according to the EU regulation and German Fertilizer Ordinance [22,23]. The same letters indicate no significant differences between a pair of fertilizers (Tukey's HSD test (α = 0.05)). Analysis of Variance: ** = $p \leq 0.01$, *** = $p \leq 0.001$. For fertilizer abbreviations, see Table 1.

Fertilizer	**Cd**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
	(mg kg^{-1} P_2O_5)	**(mg kg^{-1})**			**(mg kg^{-1})**		
SSA	3 ^{d}	0.6 ^{d}	123 ^{a}	641 ^{a}	98.8 ^{a}	129 ^{a}	3189 ^{a}
RP	7.4 ^{c}	2.0 ^{a}	45.4 ^{c}	11.6 ^{c}	25.5 ^{b}	20.0 ^{c}	97.3 ^{c}
SP-0	7.8 ^{b}	1.3 ^{b}	75.9 ^{b}	9.2 ^{c}	20.7 ^{b}	11.4 ^{d}	75.9 ^{cd}
SP-25	8.6 ^{a}	1.2 ^{c}	53.7 ^{c}	104 ^{b}	31.5 ^{b}	29.1 ^{b}	642 ^{b}
STR	<0.06 [1]	<0.06 [1]	8.4 ^{d}	1.4 ^{c}	5.0 ^{b}	<0.06 [1]	10.7 ^{d}
Analysis of Variance	***	***	***	***	**	***	***
			Maximum concentrations				
EU regulation	60.0 [2]	3.0 [3]		600	100	120	1500
German Fertilizer Ordinance	50.0 [2]	1.5 [3]		-	80	150	-

[1] below the detection limit; [2] if P_2O_5 is > 5%; [3] if P_2O_5 is < 5%.

Table 3. Calculated mean input of the elements cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) per kg phosphorus (P) (mg kg^{-1} P). For fertilizer abbreviations, see Table 1.

Fertilizer	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
			(mg kg^{-1} P)			
SSA	7.2	1380	7207	1110	1450	35,832
RP	16.6	382	97	214	168	818
SP-0	18.1	1040	126	284	157	1039
SP-25	19.3	881	1700	516	477	10,527
STR	-	70	11	42	-	89

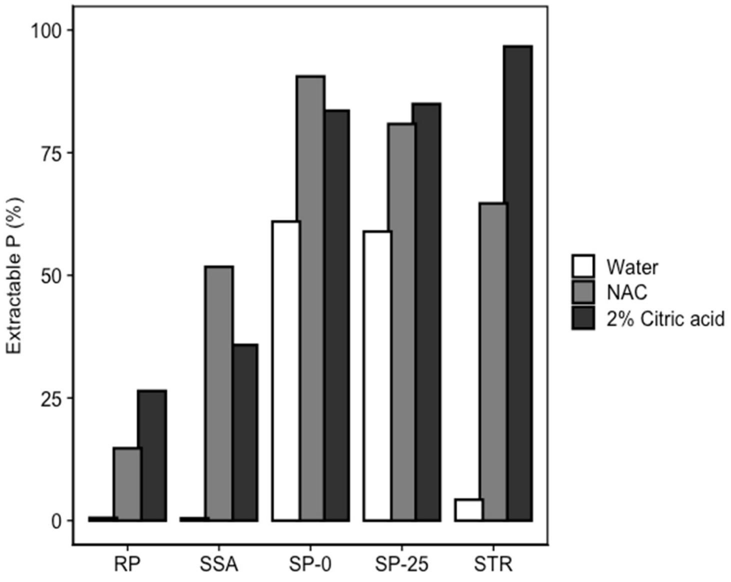

Figure 1. Phosphorus (P) extracted (% of total P) with water, 2% citric acid and neutral ammonium citrate (NAC). For fertilizer abbreviations, see Table 1.

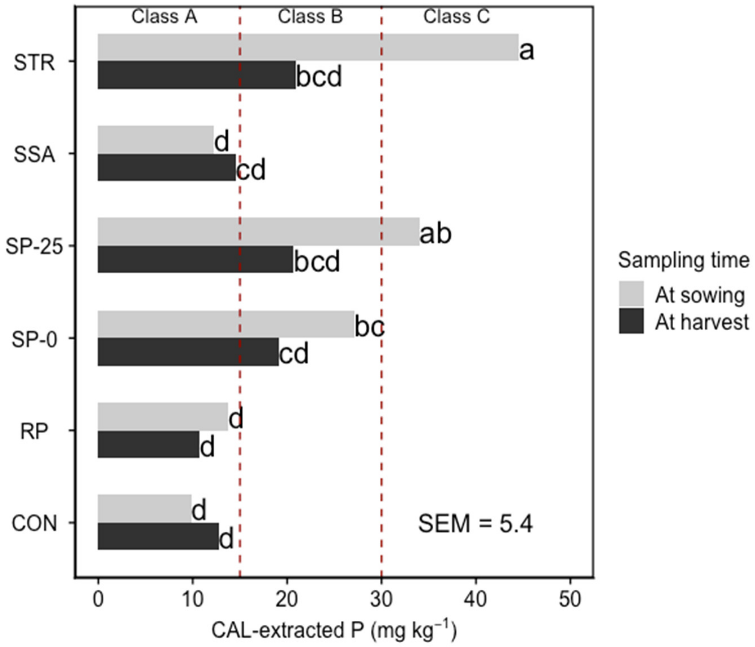

Figure 2. Mean Calcium-Acetate-Lactate extractable phosphorus (CAL-P) (mg kg^{-1}) at sowing and at harvest. Class A–C are soil plant-available P classifications for fertilization recommendation in Germany (Class A: strong need for fertilizing to Class C; Class B: need for fertilizing to Class C; Class C: only fertilize the P removal by harvest) [24]. The same letters indicate no significant differences between the treatment (n = 4, Tukey's HSD test (α = 0.05)). SEM = standard error of the mean. For fertilizer abbreviations, see Table 1.

Soil CAT-extractable Cu and Zn concentrations of all treatments were below the detection limit (1 mg kg^{-1}). Soil CAT-extractable Mg concentration was not significantly different between pairs of treatments, where STR had the highest concentration (172.4 mg kg^{-1}) (Table 4).

Only EDTA-extractable Fe concentrations were detectable in the substrate samples (Table 4), where SSA had a significantly higher concentration (220 mg kg^{-1}) than other treatments. The concentration of EDTA-extractable Fe in the SP-25 treatment was not statistically different from that in SP-0.

Table 4. Mean values of CAT-extractable magnesium (Mg) and EDTA-extractable Iron (Fe) (mg kg^{-1}) after fertilizer application. The same letters indicate no significant differences between the treatment (n = 4, Tukey´s HSD test (α = 0.05)). Analysis of Variance: *** = $p \leq 0.001$, ns = not significant ($p > 0.05$). For fertilizer abbreviations see Table 1.

Treatment	**CAT-Extraction**	**EDTA-Extraction**
	Mg	**Fe**
	(mg kg^{-1})	
CON	139.3	137 ^{bc}
SSA	145.6	220 ^{a}
RP	160.5	139 ^{bc}
SP-0	143.3	161 ^{bc}
SP-25	153.3	166 ^{b}
STR	172.4	136 ^{c}
Analysis of Variance	ns	***

3.3. Maize Growth and Aboveground Biomass Nutrient (P, Mg, Fe) Content

The STR treatment obtained the highest maize aboveground biomass among other treatments (Figure 3). SP-0 and SP-25 had 20% less aboveground biomass and similar root biomass compared to STR. All treatments except SSA had a significantly higher aboveground biomass than No-P control treatment (CON).

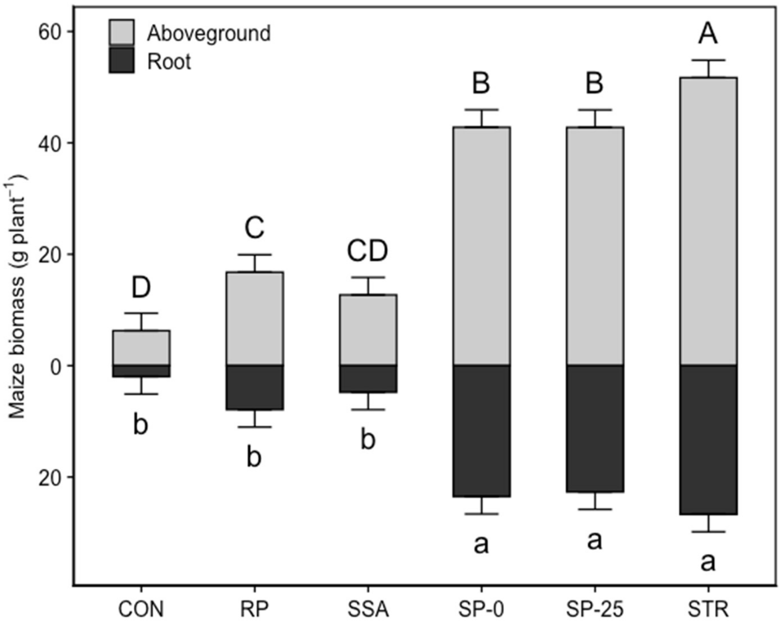

Figure 3. Mean values of maize biomass (g plant^{-1}) after 10 weeks of growth. The same letters indicate no significant differences between the treatment (n = 4, Tukey´s HSD test (α = 0.05)). Error bars indicate standard error of the mean. For fertilizer abbreviations, see Table 1.

The differences in aboveground biomass P concentrations were less pronounced than those in aboveground biomass P content (Table 5). STR had the highest P concentration of 1.1 mg kg^{-1}, which was in the same range as SP-0, SP-25, and CON. In contrast, the aboveground biomass Mg and Fe concentrations indicated a dilution effect where the lowest nutrient concentration was found in the plant with the highest biomass (Table 6).

Table 5. Mean values of maize aboveground biomass P concentration (mg kg^{-1}) and P content (mg P plant^{-1}) after 10 weeks of growth. The same letters indicate no significant differences between the treatments (n = 4, Tukey´s HSD test (α = 0.05)). For fertilizer abbreviations, see Table 1.

	P Concentration (mg kg^{-1})	**P Content (mg P plant^{-1})**
CON	0.94 ^{ab}	5.87 ^{c}
SSA	0.82 ^{b}	10.17 ^{c}
RP	0.78 ^{b}	13.06 ^{c}
SP-0	0.98 ^{ab}	41.87 ^{b}
SP-25	0.99 ^{ab}	42.44 ^{b}
STR	1.1 ^{a}	57.31 ^{a}

Table 6. Mean concentration (mg kg^{-1}) and contents (mg plant^{-1}) of magnesium (Mg), iron (Fe), cupper (Cu), zinc (Zn), cadmium (Cd), chromium (Cr), nickel (Ni) and lead (Pb) in maize aboveground biomass. The same letters indicate no significant differences between the treatment (n = 4, Tukey´s HSD test (α = 0.05)). Analysis of Variance (ANOVA): *** = $p \leq 0.001$, ns = not significant ($p > 0.05$). For fertilizer abbreviations, see Table 1.

Treatment	**Mg**	**Fe**	**Cu**	**Zn**	**Cd**	**Cr**	**Ni**	**Pb**
	Concentration (mg kg^{-1})							
CON	2674 ^{a}	53.61 ^{a}	3.84 ^{a}	14.44 ^{a}	0.10	0.22	0.50 ^{a}	0.32
SSA	2055 ^{b}	45.09 ^{b}	3.14 ^{b}	11.83 ^{ab}	0.08	0.17	0.30 ^{b}	0.23
RP	1999 ^{bc}	44.97 ^{b}	2.67 ^{bc}	10.55 ^{bc}	0.07	0.28	0.24 ^{b}	0.14
SP-0	1712 ^{bc}	26.44 ^{c}	2.06 ^{d}	6.87 ^{cd}	<0.05	0.11	0.18 ^{b}	0.34
SP-25	1681 ^{c}	27.06 ^{c}	2.08 ^{d}	9.36 ^{bcd}	<0.05	0.17	0.25 ^{b}	0.22
STR	1987 ^{bc}	27.79 ^{c}	2.24 ^{cd}	7.17 ^{cd}	<0.05	0.28	0.19 ^{b}	0.16
Directive 2002/32/EC	-	-	-	-	0.44	-	-	26.4
ANOVA	***	***	***	***	ns	ns	***	ns
	Content (mg plant^{-1})							
CON	16.78 ^{d}	0.34 ^{d}	0.02 ^{d}	0.09 ^{b}	<0.01	<0.01	<0.01	<0.01
SSA	26.10 ^{cd}	0.57 ^{c}	0.04 ^{cd}	0.15 ^{b}	<0.01	<0.01	<0.01	<0.01
RP	33.53 ^{c}	0.75 ^{c}	0.04 ^{c}	0.18 ^{b}	<0.01	<0.01	<0.01	<0.01
SP-0	73.27 ^{b}	1.13 ^{b}	0.08 ^{b}	0.29 ^{a}	<0.01	<0.01	0.01	0.01
SP-25	71.90 ^{b}	1.16 ^{b}	0.08 ^{b}	0.40 ^{a}	<0.01	<0.01	0.01	0.01
STR	102.73 ^{a}	1.44 ^{a}	0.11 ^{a}	0.37 ^{a}	<0.01	0.01	0.01	0.01
ANOVA	***	***	***	***	-	-	-	-

The aboveground biomass P content showed a similar trend to aboveground biomass (Table 5). The highest P content was found in the STR treatment, followed by SP-0 and SP-25, which generated 37% and 35% less P content, respectively, than STR. There was no significant difference among the P contents in the treatments RP, SSA, and CON. Shoot Mg and Fe contents followed the order of aboveground biomass, where STR had the most contents (Table 6). There was no significant difference between the shoot Mg and Fe contents in SP-0 and SP-25, which had considerably higher levels than in RP, SSA, and CON.

P use efficiency (PUE) of STR was the highest (5.26%) among the treatments (Table 7). Similar PUEs were found between SP-0 and SP-25. RP and SSA had nearly no efficiency on plant P accumulation.

Table 7. P use efficiency (PUE) means ± standard deviation of different fertilizer treatments. For fertilizer abbreviations see Table 1.

	RP	**SSA**	**SP-0**	**SP-25**	**STR**
PUE (%)	0.63 ± 0.11	0.38 ± 0.16	3.57 ± 0.50	3.47 ± 0.73	5.26 ± 0.84

3.4. Aboveground Biomass PTE Content under Different Fertilizer Treatments

In aboveground biomass Cu, Zn, and Ni concentrations, significant differences were found among the treatments (Table 6). STR, SP-0, and SP-25 resulted in less Cu, Zn and Ni concentrations than CON in aboveground maize biomass, indicating a dilution effect due to the relatively larger biomass. SP-0 and SP-25 were in the same range for the selected PTE concentrations. The maximum concentrations of Cd and Pb in animal feed according to the EU directive [25] were also listed in Table 6. The concentrations of Cd and Pb were in compliance to the regulatory limits. Cu and Zn content in aboveground maize biomass for six treatments showed the same trend as aboveground biomass. Cd, Cr, Ni, and Pb accumulation in plants of all treatments were less than 0.01 mg plant^{-1}.

4. Discussion

4.1. Limitation of SSA as a Secondary Raw Material in P Fertilizer Production

The concentrations of Cd, Ni, and Pb in the tested sewage sludge ash (SSA) were greater than the data provided by the SSA producer KOPF SynGas © (Table S1), indicating the inconsistency of the element mass fractions in tested SSA. The PTE concentrations in sewage sludge can show considerable fluctuations with time, especially for Pb and Cd, which are further concentrated in SSAs [9]. It is suggested that monthly or annual mean concentration of PTEs is more suitable than single sampling to evaluate the contamination risk.

According to the current EU Fertilizing Product Regulation and the German Fertilizer Ordinance, only SSA that was used to produce SP-25 exceeded the maximum concentration of Cu, Ni, Pb, and Zn (Table 2). As SSA might be categorized as 'thermal oxidation materials or derivates' of the component material in the coming updated EU Fertilizing Product Regulation, the direct use of SSA as a P fertilizer or as a secondary raw material to produce fertilizer may therefore be forbidden. The relatively high Cu, Ni, Pb, and Zn concentrations was also observed in some SSAs produced in Germany due to the input of industrial sludge [6]. For many of the existing mono-incineration plants, further treatment is required to reduce contaminant concentrations before the use of SSAs in fertilizer production.

The precipitating agents used during wastewater treatment may also affect the feasibility of using SSA to produce P fertilizers. Iron or aluminum compounds are often used in the third purification stage of wastewater treatment to remove P by forming water-insoluble compounds, which remains in the sludge and concentrated in SSA. The SSA used in the SP production was from sludge, which was produced using an iron compound as a precipitating agent. A previous study found that, regardless of the acid concentration during acidulation, iron-based SSA yielded less processable products than aluminum-rich SSA on plant scale concerning the physical properties of delivered product [26]. Since SP-25 was produced in a small amount on lab scale, it was easy for the delivered product to be further processed to fine particles. Furthermore, iron-based SSA required less amounts of acid than aluminum-rich SSA for complete extraction of P, which implied less resource consumption to achieve high P availability [27].

Concerning the fertilizer P concentration, the value for SP-25 (61 mg g^{-1}) is barely higher than the required value (52 mg g^{-1}) for straight solid inorganic macronutrient fertilizer in the EU Fertilizing product regulation [23]. The low P content of SP-25 can be attributed to the low P content of SSA (89 mg g^{-1}) and higher sulphuric acid input per unit P for SSA than for RP during the SP production process. One possible solution is partially replacing RP with SSA in triple-superphosphate production where phosphoric acid is used instead of sulphuric acid to reduce the PTE to P ratio. However, the resulting product was found to be difficult to process due to coagulation problems during the acidification of SSA using phosphoric acid [26]. Another possible solution is the separation of industrial and municipal sludge in the incineration plant. In Germany, 52% of SSA was produced from the mixture of municipal and industrial sludge, and most of them were incinerated in large facilities [28]. Mass flow management for separating municipal and industrial sludge in those facilities will increase the P content and reduce heavy metals in their SSA, which enables a wide use of SSA in fertilizer production.

4.2. P Availability of Produced Superphosphates

The soil–sand substrate itself can be categorized as very low in plant-available P according to the German fertilization recommendation (Class A, <10 mg P_{CAL} kg^{-1}) [24]. After fertilizer application at sowing, less than half of the total P input through the fertilizers was able to be extracted from the substrate (Figure 2). Although the P input in this study was extremely high (equivalent to 312 kg P ha^{-1}), only STR and SP-25 built up soil plant-available P concentrations to an optimal level (Class C: 15–30 mg P_{CAL} kg^{-1} soil) where a field soil does not need additional input from fertilization apart from the amount of P removed by the harvested crop. This increase of the CAL-extractable P fraction of the substrates after SP-0 and SP-25 application compared to the application of RP and SSA is consistent with the assumption that concentrated sulphuric acid enhances the P-availability of RP and SSA. The same range of CAL-extractable P in substrates applied with SP-0 and SP-25 and their extractable P fractions in water and organic acids indicated that two SPs had a similar pattern of P dissolution in the substrate after fertilizer application and after plant uptake.

P use efficiency of the treatments corresponded to the soil CAL-extractable P results. SSA and RP had almost no P use efficiency for plants, as expected from other studies [29,30]. The crystalline P-compounds in the tested SSA are mainly $Ca_3Mg_3(PO_4)_2$ [10], which are not immediately available for plant uptake. Acidulation of SSA with concentrated sulphuric acid may lead to the formation of plant-available mono-calcium phosphate, which shows some similarity to the acidulation of RP. Both SP-0 and SP-25 significantly increased maize biomass yield and P content compared to CON by the same order of magnitude. Hence, the 25% replacement of RP by SSA in SP-25 did not have an adverse impact on its plant-availability. In a previous study using the same SSA, only 11% SSA replacement in SP production achieved the maize biomass and P content to the same level as traditional SP, whereas increased SSA replacement significantly impaired the growth of maize [10]. The higher amount of acid relative to P in SSA (5.6 mL g^{-1} P) during our SP-25 preparation may have improved the P availability in our SP-25 compared to that SP, where 1.6 mL sulphuric acid was applied per g P of SSA. However, this increased input of sulphuric acid diluted the P content in the resulting product to 6.1%. Therefore, unless an increased P content in SSA is obtained, its application in SP production should be limited to a fraction that enables the required P concentration according to EU regulations to be reached.

4.3. PTE Content in Aboveground Biomass

The growing condition for maize in the greenhouse experiment can be considered as an extreme case for PTE accumulation due to the high fertilization dose (equivalent to 312 kg P ha^{-1}) and the intensive rooting in the pot, especially for Cd, which is relatively mobile in soil compared to the other PTEs. Aboveground maize Cd concentration of the SP-25 treatment was below the detection limit, although its Cd input was the highest among all the treatments (19.3 mg kg^{-1} P). It is possible that most of the assimilated Cd in maize was concentrated in the root and not translocated to the shoot and grain, which is one of the plant defense mechanisms to prevent injuries induced by heavy metals [31,32]. Furthermore, the low pH of the substrate (pH_{CaCl2} 5.6) may suppress Cd uptake by plants due to competition with other metallic cations and hydrogen ions, even though it favors the mobility of Cd in soil [33,34]. Zn in soil could also affect Cd's mobility and its uptake by the plant by inhibiting the uptake of Cd by competing with the same membrane transporter [35,36]. In this study, Zn input per unit of P from SP-25 application was 10 times higher than from SP-0 (Table 3). However, EDTA- and CAT-extractable Zn in the substrate fertilized with SP-25 indicated low Zn bioavailability. Relatively low Zn bioavailability to plants and bio-accessibility to humans in ingested soil were also reported in SSA and in the leachate of SSA using 0.5 M sulphuric acid [37,38]. It is possible that, during the gasification of sewage sludge, ZnO was the dominant Zn species under the combustion temperature of 870 °C after desulfurization, which is not immediately available for plants [39]. This assumption needs to be further proved by X-ray diffraction analysis. Nevertheless, our plant and soil extraction results indicated that the excessive input of Zn from SP-25 to soil is unlikely to influence plant Cd uptake.

Pb accumulation in aboveground maize by the application of SP-25 was within the same level as SP-0. The relatively extensive input of Pb from SP-25 (477 mg kg^{-1} P) compared to SP-0 (157 mg kg^{-1} P) did not result in greater Pb accumulation in maize shoot, probably due to Pb's low mobility in soil [34]. Only in severely Pb-contaminated soil Pb was found to be more highly concentrated in maize roots than in other plant parts, where 10–15% of Pb concentration in soil was transported to maize roots [40]. In the greenhouse experiment, the Pb input was much lower than the background value in a heavily contaminated soil. Thus, the Pb accumulation in maize root was of little importance in this study, and it is assumed that most of the Pb from SP-25 was retained in the soil.

4.4. PTE Accumulation in Soil

The accumulation of PTE in the soil is determined by the inputs and outputs via different sources. The anthropogenic input through atmospheric deposition and intensive fertilization in arable land could pose a risk to human health during the bioaccumulation along the food chain. The PTE to P ratio of a fertilizer is considered the main driving factor for contaminant flows in soil [41,42]. Results showed that SP-25 contributed the highest Cd input per unit P due to its relatively low P concentration (61 mg g^{-1}). In the greenhouse experiment, the input of Cd, Cu, Ni, Pb, and Zn from SP-25 was larger than from SP-0. However, PTE solubility and bioavailability rather than the total input in the soil are the key factors in evaluating the potential risk. All of the analyzed PTEs (Cd, Cr, Cu, Pb, Ni, Zn) extracted by the CAT and EDTA method showed concentrations below the detection limit, indicating their low bioavailability in the soil.

The output of soil PTEs includes crop removal, surface runoff, and leaching. Results showed that only a small proportion of PTE output was derived from crop removal. Most of the PTE inputs were retained in soil inactively. Those remaining PTEs could be leached out or lost as runoff from the surface, which potentially may cause contaminations of water bodies. Leaching of PTEs from soil largely depends on its solid-soil solution partitioning, which is often related to soil properties like pH, soil organic matter and clay content, and total element concentration [43]. The low bioavailability of PTEs could result in a gradual accumulation in soil by repeated application of SP-25. It may further change the solid-soil solution partitioning due to enlarged soil total element concentration in the long term. This may be of concern especially for Cu, Ni and Pb, which had much higher inputs with SP-25 application compared to SP-0, but less for Zn. High P application in Zn-deficient soil could induce plant Zn deficiency in association with restricted root Zn uptake and arbuscular mycorrhizal colonization [44,45]. The Zn input from SP-25 may alleviate plant Zn deficiency by gradually increasing the soil solution Zn concentration.

Cd concentration in SP-25 and SP-0 were significantly different from each other, but their input difference was small (1.2 mg kg^{-1} P). In addition, the mean concentration of Cd in SP-25 (8.6 mg kg^{-1} P_2O_5) was much smaller than the concentration in three SPs sold in Germany (105 mg kg^{-1} P_2O_5) [3]. Ref. [42] also estimated less Cd input via SSA than via phosphate rock (RP) and triple superphosphate (TSP) after 200 years of fertilization (11 kg P ha^{-1} year $^{-1}$) by a mass balance approach. The replacement of SSA in SP production may reduce the Cd contamination risk posed to the soil.

5. Conclusions

Results showed the agronomic potential of using sewage sludge ash (SSA) in superphosphate (SP) production. The application of SP-25 that was produced with a 25% replacement of rock phosphate (RP) by SSA led to a satisfactory aboveground biomass yield and nutrient content while keeping the PTE contamination in maize plants below the EU limit for animal feed. Nonetheless, the Pb, Cu, and Zn concentrations in tested SSA exceeded the maximum limit set by the EU fertilizing Products Regulation, which restricts its use as a secondary raw material in P fertilizer production.

The relatively high inputs of Cu, Ni and Pb by the application of SP-25 may decrease solid-soil solution partitioning and result in accumulation in soil and water bodies. Separation of municipal/industrial sludge may facilitate minimizing the PTE concentration in SSAs. Efficient removal of excessive Pb, Cu, and Zn in tested SSA might be achieved by advanced technology, such as thermochemical process with chlorides or Na/K additives at a temperature over 950 °C [9,46]. Separation of volatile heavy metals like Zn, Pb, Cd, and Hg via gas phase at a high bed temperature during the incineration of sewage sludge or post-treatment of SSA could increase the value and reduce the risk associated with SSA-based fertilizer [9]. In general, the use of SSA in P fertilizer production is promising to achieve a high P recovery from sewage sludge without compromising crop yield. However, long-term studies under field conditions are required to evaluate the P use efficiency and contamination risk of the application of SP-25 to soil and crops.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/agronomy11081506/s1, Table S1: Cadmium (Cd), chromium (Cr), nickel (Ni) and lead (Pb) concentration in SSA dry matter (mg kg^{-1}). Data are provided by [13].

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5. Chapter III

Yield response of maize as affected by struvite placement and residual effects on subsequent crops

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Abstract

***Background**:* In fields, fertilizer placement is implemented to optimize short-term nutrient availability to crops by the precise placing of fertilizers close to the seeds. This may promote the P acquisition of plants from struvite during the early growth stage concerning its low dissolution in soil, especially in granular form.

Aims: This study investigated the direct and residue effects of the fertilizer application method (placement vs broadcasting) on crop yield and P content using struvite as a P fertilizer in comparison to DAP.

Methods: Field experiments with maize (*Zea mays* L.) were conducted over 2 years in two adjacent fields in southern Germany. Triticale (*Triticosecale Wittm. ex A. Camus.*) and faba bean (*Vicia faba*) were grown as subsequent crops after the maize cultivation to evaluate the residual effect of P fertilization from the previous year.

Results: Two-year maize results showed that placed struvite led to more than 30% higher yield and P content than broadcast applied struvite, demonstrating the strong impact of the application method. Compared to placed DAP, placed struvite led to similar yields and P use efficiencies (9-10%). The yield and P content of triticale and faba bean indicated a comparable availability of residual P from DAP and struvite. In comparison to triticale, faba bean failed to take up more P from struvite as expected.

Conclusions: The present study demonstrated that struvite applied by placement is an effective P source and is promising to replace DAP in maize cultivation.

1. Introduction

Besides limited indigenous Phosphorus (P) from the parent rocks, mineral fertilizers are the major P sources for crops. Most of the mineral phosphate fertilizers are manufactured from phosphate rock, an EU-listed critical raw material, which is non-renewable, non-substitutable, and geographically restricted to a few countries (European Commission, 2020). As the rate of phosphate rock mining exceeds its generation rate (Chowdhury et al., 2017), alternative P sources are crucial to mitigate the dependency on the limited natural resource and to further ensure future global food security. In the EU, around 18% of P losses ended up in communal sewage sludge (van Dijk et al., 2016), showing a great potential to partially substitute the P from phosphate rock with P from sewage sludge. Several technologies have been developed to retrieve P from sewage sludge and to synthesize P-rich fertilizer products that are available for plant uptake (Gorazda et al., 2017; Herzel et al., 2016; Meyer et al., 2019; Takahashi et al., 2001). Basically, they can be divided into three categories: precipitated phosphate salts and derivatives, thermal oxidation materials or derivatives, pyrolysis and gasification materials (Huygens et al., 2019). Among various P-rich products generated from sewage sludge, struvite ($NH_4MgPO_4 \cdot 6H_2O$) as a precipitated phosphate salt, is recognized as an effective P fertilizer that can compete with phosphate rock derived fertilizers such as single superphosphate (SSP), triple superphosphate (TSP) and ammonium phosphates (Hertzberger et al., 2020; Muys et al., 2021). Besides recycling from sludge, struvite derived from biogas digestates and animal slurry is also an effective alternative to TSP (Bach et al., 2022; Cerrillo et al., 2015). Although diammonium phosphate (DAP) has a higher ammonium to P ratio than struvite, it is an obvious reference fertilizer considering its solution pH similar to struvite and its high consumption in Europe (IFA, 2018). A previous study found a comparable wheat yield and P recovery for struvite and DAP in a 90-day pot experiment (Talboys et al., 2016). However, the shorter growth period (36 days) resulted in 39% less wheat P uptake from struvite than from DAP in the same study. The low water solubility of struvite leads to a slower P diffusion in soil compared to water-soluble phosphate rock-derived fertilizers, especially when applied in a granular form (Degryse et al., 2017). Struvite is regarded as a slow-release fertilizer that fails to provide enough P to plants during early growth, and therefore blends with water-soluble P fertilizer are recommended (Hertzberger et al., 2021). Besides struvite blending, methods that can lead to a faster dissolution are also proposed, such as creating an acidic environment around the struvite granule either in low pH soils (Degryse et al., 2017) or in the rhizosphere of plants as a result of root exudates (Robles-Aguilar et al., 2019). Accordingly, legumes with particularly pronounced P-mining strategies as a result of strong exudation of organic anions and protons in the rhizosphere are likely to induce the P release from struvite.

The application method also influences the plant's response to different fertilizers. Especially for recycled fertilizers which are often insoluble in water, the application method may influence the dissolution of recycled fertilizers by affecting the contact surface between soils and fertilizers. For instance, incorporating sewage sludge ash in the soil led to more than doubled yield and P uptake of maize than placed closed to seed in a pot experiment (Lemming et al., 2016), where the incorporation is likely to enlarge the potential reaction area between the ash and the soil and further induce the dissolution of acid-soluble P fractions in the ash. However, the impact of the application method is also related to the particle size of the fertilizers. For struvite with a larger particle size (3 mm diameter), no effect of the application method was found on maize biomass and P uptake under greenhouse conditions (Hertzberger et al., 2021). Whether a consistent result can be found under field conditions is unknown.

To date, only a few published studies on the fertilizer efficiency of struvite were conducted under field conditions, where the conclusions were inconsistent (Gell et al., 2011; Vogel et al., 2017; Wollmann & Möller, 2018). A thorough review of struvite fertilizer efficiency argued that a P responsive soil should be used to exclude a strong P supply from the soil (Hertzberger et al., 2020), which might explain the inconsistent conclusions from field studies. Moreover, in those field studies, more than half of the applied P from struvite was retained in the soil after the first cropping season (Vogel et al., 2017; Wollmann & Möller, 2018) contributing to the P nutrition of the following crop. The pattern of dissolution and diffusion in soil differs between struvite and water-soluble fertilizers and can affect their P immobilization during the cropping season and have different residual effects on the following crop.

In this study, a two-year field experiment was conducted in two adjacent fields in Southern Germany. Maize was cultivated in one field in 2020 and in an adjacent field in 2021. Faba bean and triticale were cultivated after maize as subsequent crops. The objectives of this study were: 1) to evaluate the efficiency of struvite compared to DAP as affected by placed vs. broadcast fertilizer application to silage maize, and 2) to investigate the residual effect of struvite and DAP on the P nutrition and growth of faba bean and triticale as subsequent crops. We hypothesize that 1) placement can enhance maize yield and P use efficiency of struvite compared to broadcasting, 2) under fertilizer placement, struvite can achieve a similar yield and P use efficiency as DAP in maize cultivation, and 3) faba bean as legume can take up more P from residual struvite than from residual DAP.

2. Materials and methods

2.1 Experiment site

The field experiment was conducted in two adjacent fields at Oberer Lindenhof in St. Johann, Eningen unter Achalm, Germany (48.2 ºN, 9.1 ºE). During the growing season, the mean temperatures were 15.1 ºC and 14.5 ºC and the annual precipitations were 386.1 mm and 493.4 mm in 2020 and 2021 respectively. The soil of the field site is a silty loam soil with 933 mg kg^{-1} total P, 9 mg kg^{-1} of P_{CAL} (VDLUFA, 2012), and a soil pH_{Cacl2} of 5.1. The soil CAL-extractable P status is categorized as class A (very low < 15 mg P_{CAL} kg^{-1} soil) based on the regional fertilization recommendation, implying a strong need for P fertilization (Wiesler et al., 2018). The site was previously managed as maize monocropping without any P fertilization two years before the field experiment.

2.2 Experimental design and field management

Two factors with two levels were tested in the field experiment: fertilizer type (struvite and DAP) and application method (placed and broadcast). The treatments were as follows: no-P (control), DAP-placed, DAP-broadcast, struvite-placed, and struvite-broadcast. The field experiment was arranged in a Latin-square design and consisted of five east-west blocks and five north-south blocks. Between two adjacent east-west blocks, there was a 3 m border. Each plot was 9 m wide and 11 m long.

9 Mg ha^{-1} of dolomitic lime (75% $CaCO_3$) was incorporated into the field in November 2019, followed by 750 kg ha^{-1} of compound K fertilizer Korn Kali® (33% K, 3.6% Mg, 5% S, 3% Na). The soil pH_{CaCl2} after liming was 6. Soil mineral nitrogen (N_{min}) was determined in 0-30, 30-60, and 60-90 cm soil depths in each east-west block on the 8th of April in 2020 and on the 10th of May in 2021, which ranged between 65-114 kg N ha^{-1} in 2020 and between 71-89 kg N ha^{-1} in 2021. Maize (cultivar. Stabil) was sown on the 19th of May 2020 with a row spacing of 75 cm and plant spacing of 12 cm using a single seed sowing machine equipped for placed starter fertilizer application (Rau Maissägerät, Unisem, RAU Landmaschinen GmbH, Korntal-Münchingen, Germany). For treatments with fertilizer placement, the horizontal fertilizer band was located 6-8 cm below the seed. For treatments with broadcast fertilization, the fertilizer was broadcast applied and incorporated at 10 cm soil depth before sowing. Struvite fertilizer was produced by The Stuttgart Process (Meyer et al., 2019) and it contained 11% P, 4.8% N, and 8.8% Mg with a granular size of 3-5 mm. Commercial DAP fertilizer (Triferto Fertilizers) contained 20% of P and 18% of N with a granular size of 3-3.5 mm. Except for no-P control treatment, all treatments received 85 kg ha^{-1} P at sowing which was based on a

German fertilization recommendation (Wiesler et al., 2018). On the 9th of July 2020 and on the 14th of July 2021, when most of the plants were at the 7-leaf (V7) stage, additional N was broadcasted by hand as urea with urease inhibitor (PIAGRAN® pro, 46% N) to all treatments. According to the German regulation on the use of N fertilizer, the amount of N fertilizer was calculated based on the yield expectation on the site, the soil N_{min} content, and the N contained in the P fertilizer. On the 7th of October 2020, aboveground maize was harvested using a plot combine harvester (Silager SF2000, BAURAL, Blois, France) in the two central rows per plot, where a 1 m border of maize from each side was removed beforehand. A sub-sample of chopped maize was collected from the field, weighed, and dried at 60 ºC until a constant weight was obtained. After the harvest of maize, soil tillage was conducted at 10 cm soil depth. On the 14th of April 2021, faba bean (cultivar. Fanfare) was sowed on one half of each plot, and triticale (cultivar. Somtri) was sowed on the other half of each plot together with 120 kg ha^{-1} N as calcium ammonium nitrate. On the 25th of August 2021, 1 m^2 of faba bean and triticale were harvested by hand in each plot. Grain and plant material were separated, and sub-samples were further processed for nutrient content analyses. In the adjacent field, the same experimental design with maize was repeated in 2021. Maize seed was sown on the 1st of June and the aboveground biomass was harvested on the 20th of October using the same machinery as in 2020. Due to a sowing mistake, two plots in the second block were omitted in 2021. After the harvest of maize, the same experimental setting with faba bean and triticale was conducted in April 2022 and harvested in August 2022. 0.5 m^2 of aboveground biomass was harvested and sub-samples were further processed for nutrient content analysis.

2.3 Sampling and laboratory analysis

All plant samples were milled and digested in aqua-regia solution (VDLUFA, 2011). P concentrations in the solutions were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Plant P offtake was calculated as the product of plant P concentration and yield. The fertilizer P use efficiencies (PUE) for the year of fertilization were calculated using the following equation:

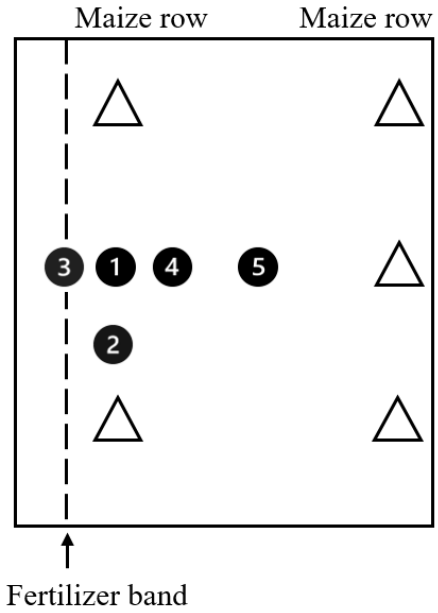
$$\text{PUE (\%)} = \frac{Plant\ P\ offtake\ (treatment)\ -\ Plant\ P\ offtake\ (control)}{P\ applied\ by\ fertilization} \times 100\%$$

The Harvest index (HI) of triticale and faba bean was calculated using the following equation:

$$\text{HI} = \frac{Grain\ yield}{Aboveground\ biomass}\ (\text{kg kg}^{-1})$$

Soil samples were taken to 30 cm depth before sowing in 2020 and after the harvest of triticale and faba bean in 2021. Nine samples were randomly sampled per plot, homogenized, air-dried, and passed through a 5 mm mesh sieve. Soil CAL-P extraction was measured (VDLUFA, 2012).

Data on maize roots were determined by roots in sampled soil columns. Soil columns were taken on the 13th of July 2020, using a plastic cylinder with a height of 30 cm and a volume of 588 cm^3 (Supplemental Figure S1). Samples were taken at five positions around one maize plant (Figure 1) in three blocks. Position 3 included the fertilizer band in the treatments with placed application. In the control and broadcast treatments, samples were taken in equivalent reference positions. After the sampling, each soil column was divided into three parts, representing 0-10, 10-20, and 20-30 cm soil depth. Roots in the soil column were picked out by hand, washed, and stored in a 70% ethanol solution for preservation. Cleaned root samples were scanned and further analyzed with WinRHIZO (Regent Instruments Inc., Quebec, Canada) software for root length. Root density (cm cm^{-3}) was calculated by the root length divided by the soil volume. No visible root was found in some samples therefore a statistical analysis of the root length was not performed.



Position	**Description**
1	Underneath the maize plant
2	In the middle of two adjecent maizes
3	Fertilizer band
4	Opposite to the fertilizer band
5	In the middle of two maize rows

Figure 1. Illustration of root sampling position 1-5 and their descriptions. Green triangles represent single maize plants. The yellow dotted line represents the fertilizer band which was 5 to 8 cm beneath the soil surface.

2.4 Statistical analysis

Statistical analysis and graphical presentation were conducted using the R environment (R Core Team, 2021). After verifying the homogeneity of variance, a one-way analysis of variance (ANOVA) model was used with the treatment as the factor and an error term for the replication in blocks to evaluate their effect on the crop yield and P offtake. A two-way ANOVA was performed for the P use efficiency, where fertilizer and application method were factors. When a significant effect was found, multiple comparisons of treatments were conducted using Tukey’s Honestly Significant Difference test. Comparisons of estimated marginal means for contrasts of interest were performed using defined contrasts with t-tests.

3. Result

3.1. Yield, P concentration, and P offtake of maize

In 2020 and 2021, DAP-placed and Struvite-placed had the highest yield of aboveground maize, followed by DAP-broadcast, the control and Struvite-broadcast (Table 1). No significant difference was found between DAP-placed and struvite-placed. The P concentrations of aboveground maize were 1.8 to 1.9 g kg^{-1} in 2020 and between 1.6 to 1.7 g kg^{-1} in 2021, whithout significant difference between treatments. The highest P offtake by maize was found after DAP-placed and struvite-placed fertilization, both of which were significantly higher than the other treatments.

The control treatment resulted in significantly reduced yields and P offtakes compared to the other four P treatments in both years. DAP only significantly increased the yield of maize in 2020 compared to Struvite. The positive effect of fertilizer placement was significant on yield and P offtake in both years.

Table 1. Maize yield (aboveground biomass dry matter), P concentration, and P offtake in the treatments in 2020 and 2021. The same letters indicate that no significant difference was found according to Tukey's test (α = 0.05). SEM represents the standard error of the mean. Contrasts of interest are the differences in the estimated marginal means between two treatments of interest.

Treatment	**Yield**	**P concentration**	**P offtake**
	Mg ha^{-1}	g kg^{-1}	kg ha^{-1}
	2020		
Control	12.4 c	1.8	22.6 b
DAP-broadcast	14 bc	1.8	25.6 b
DAP-placed	17.3 a	1.8	30.7 a
Struvite-broadcast	11.9 c	1.9	22.4 b
Struvite-placed	15.8 ab	1.9	30.7 a
SEM	0.39***	0.05	1.36**

	T-test		
Contrasts of interest			
Control - P treatment	-2.29**	-	-4.76*
DAP - Struvite	1.80**	-	0.94
Broadcast - Placed	-3.59***	-	-6.71***
	2021		
Control	10.6 b	1.6	16.5 b
DAP-broadcast	11.0 b	1.7	18.7 b
DAP-placed	15.2 a	1.7	26.0 a
Struvite-broadcast	11.1 b	1.6	18.3 b
Struvite-placed	15.4 a	1.6	25.0 a
SEM	0.44***	0.06	1.33**
	T-test		
Contrasts of interest			
Control - P treatment	-2.55***	-	-5.50***
DAP - Struvite	-0.19	-	0.66
Broadcast - Placed	-4.23***	-	-6.98***

*Significant at the .05 probability level. **Significant at the .01 probability level. ***Significant at the .001 probability level.

3.2. Yield and P offtake of faba bean and triticale

Yield, harvest index, P concentration, and P offtake of triticale in 2021 are listed in Table 2. Significant differences between treatments were only found in grain yield, grain P offtake and total P offtake. The highest grain yield was obtained by DAP-placed and struvite-placed treatment (both at 1.4 Mg ha^{-1}), which were significantly higher than the control (1 Mg ha^{-1}). Similarly, the treatments DAP-placed and struvite-placed had the highest grain P offtake and total P offtake, which were significantly higher than the control. In 2022, some treatments had a smaller sample size due to the loss of samples. The statistical result should be therefore treated with caution. For triticale, no significant difference between treatments was found in total yield, total P concentration, and total P offtake (Supplemental Table S1).

Table 2. Grain and total yield, harvest index (HI), P concentration and P offtake of triticale in 2021. The same letters in a column indicate no significant differences (Tukey's test, $\alpha = 0.05$).

	Yield		HI	P concentration		P offtake	
	Grain	Total		Grain	Total	Grain	Total
	Mg ha^{-1}		kg kg^{-1}	g kg^{-1}		kg ha^{-1}	
Control	1.0 b	4.9	0.21	6.2	2.4	6.3 b	11.5 b
DAP-broadcast	1.4 ab	6.4	0.22	6.4	2.6	8.9 ab	16.8 a
DAP-placed	1.4 a	5.9	0.27	6.4	2.8	9.2 a	15.6 ab
Struvite-broadcast	1.2 ab	6.3	0.19	6.4	2.4	7.5 ab	14.8 ab
Struvite-placed	1.4 a	6.4	0.22	6.5	2.6	9.3 a	16.4 a
p-value (ANOVA)	<0.05	0.16	0.1	0.67	0.3	<0.05	<0.05

Table 3. Grain and total yield, harvest index (HI), P concentration and P offtake of faba bean in 2021. Same letters in a column indicates no significant differences (Tukey's test, $\alpha = 0.05$).

	Yield		HI	P concentration		P offtake	
	Grain	Total		Grain	Total	Grain	Total
	Mg ha^{-1}		kg kg^{-1}	g kg^{-1}		kg ha^{-1}	
Control	0.9 b	2.3 b	0.39	5.8	3.3	5.2 b	7.6 b
DAP-broadcast	1.4 a	3.2 a	0.43	6.0	3.9	8.2 ab	12.3 ab
DAP-placed	1.4 a	3.3 a	0.43	6.2	4.3	8.8 a	14.3 a
Struvite-broadcast	0.9 b	2.3 b	0.37	6.8	4.0	5.9 ab	9.3 ab
Struvite-placed	1.2 ab	3.0 a	0.41	6.3	4.0	7.7 ab	11.9 ab
p-value (ANOVA)	<0.05	<0.05	0.29	0.15	0.10	<0.05	<0.05

For faba bean in 2021, significant differences between treatments were found in the aboveground biomass, grain yield, and P offtake (Table 3). DAP-placed treatment had the highest grain yield and P offtake in grain and in total, followed by DAP-broadcast and struvite-placed, however, without any significant difference. In 2022, a significant difference between treatments was found only in total P concentration, where DAP-placed had the highest concentration (2.6 g kg^{-1}) (Supplemental Table S2).

3.3. P use efficiency

For maize in both experimental years 2020 and 2021, the placement of P fertilizer led to a significantly higher P use efficiency (PUE) than broadcast application (Table 4). The Struvite-broadcast treatment even had a slightly negative value, meaning its P offtake was less than that of the control. No significant differences in PUE between fertilizer types were found.

Table 4. P use efficiency (%) of the treatments in maize.

Treatment	**2020**	**2021**
DAP-broadcast	3.5	2.6
DAP-placed	9.5	11.1
Struvite-broadcast	-0.2	2.2
Struvite-placed	9.6	10.0
	p-value (ANOVA)	
Fertilizer type	0.47	0.56
Application method	<0.05	<0.05
Interaction	0.47	0.79

To investigate the residual effect of P fertilization, the PUE of the two cropping systems after two years is shown in Table 5. In the maize-triticale system, the highest PUE was found in struvite-placed treatment with 15.3%, followed by DAP-placed treatment with 14.4%. The lowest PUE was under struvite-broadcast treatment with only 3.7%.

In the maize-faba bean system, the PUE followed the order: DAP-placed (17.4%), struvite-placed (14.6%), DAP-broadcast (9.2%), and struvite-broadcast (1.8%). In both systems, the application method significantly affected the PUE, not the fertilizer type. No interaction between the fertilizer type and the application method was found.

Table 5. P use efficiency (%) of treatment on maize-triticale and maize-faba bean cropping system. Data on maize was obtained in 2020, data on faba bean and triticale was obtained in 2021.

Treatment	**Maize-triticale**	**Maize-faba bean**
DAP-broadcast	9.7	9.2
DAP-placed	14.4	17.4
Struvite-broadcast	3.7	1.8
Struvite-placed	15.3	14.6
	p-value (ANOVA)	
Fertilizer type	0.39	0.08
Application method	<0.05	<0.05
Interaction	0.24	0.42

3.4. Soil P test of the struvite-fertilized soil after two cropping seasons

The soil CAL-P before the beginning of the trial was 9 mg P kg^{-1} soil, representing a very low soil available P concentration (Class A). After the harvest of triticale, no significant difference was found in soil CAL-P (p=0.32) between the different fertilizer treatments, but a tendency towards increased CAL-P compared to the control. Most of these still belonged to ”Class A” in the German soil P classification system, meaning excess P fertilizer should be applied than the estimated crop P removal (Figure 2A). Only under DAP-placed treatment, the soil was categorized as ”Class B” (low).

No significant difference was found in soil CAL-P (p=0.191) between treatments after faba bean harvest (Figure 2B). However, struvite-placed and struvite-broadcast treatments tended to increase the soil CAL-P to Class B, which was 2.4 and 1.8 times higher than the original soil CAL-P (9 mg P kg^{-1} soil). The soil CAL-P level under the DAP-placed and DAP-broadcast treatments still belongs to ‘Class A’. Despite the P removal by maize and faba bean, the soil in the control treatment showed a slight increase of CAL-P from 9 to 9.9 mg P kg^{-1} soil.

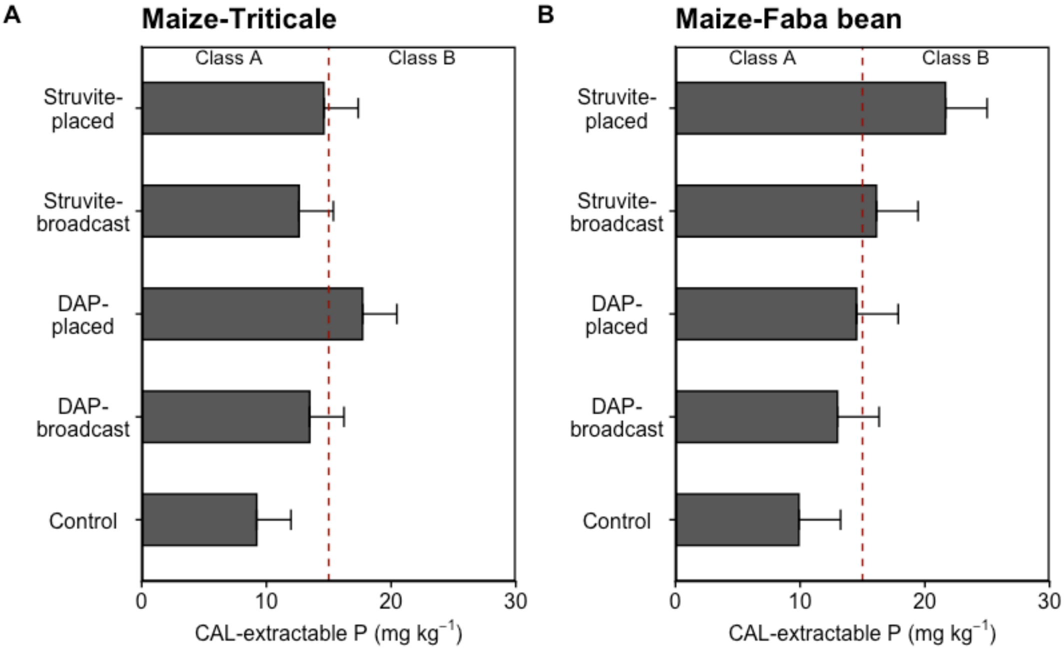


Figure 2. Soil calcium acetate lactate extractable P concentration (CAL-P, mg P kg^{-1}) after maize-triticale (A) and maize-faba bean (B) cropping. Error bars indicate the standard error of the mean. The stippled line separates CAL-P class A (very low) and class B (low) due to the German recommendation system.

3.5 Root density at different sampling positions

Figure 3 shows the maize root density at 5 sampling positions and at 3 soil depths under different treatments. The bars were stacked to present the total root density in the collected samples under each treatment at each soil depth. Most of the sampled roots were found at the top 10 cm soil depth. The root right below the maize (position 1) contributed the most to the total sampled root length at 0-10 cm soil depth, except for DAP-placed. Differences in root densities between the treatments were mainly due to differences in the sampling positions 1 and 3. Treatments with placed fertilization always showed a higher root density than the treatments with the broadcast application.

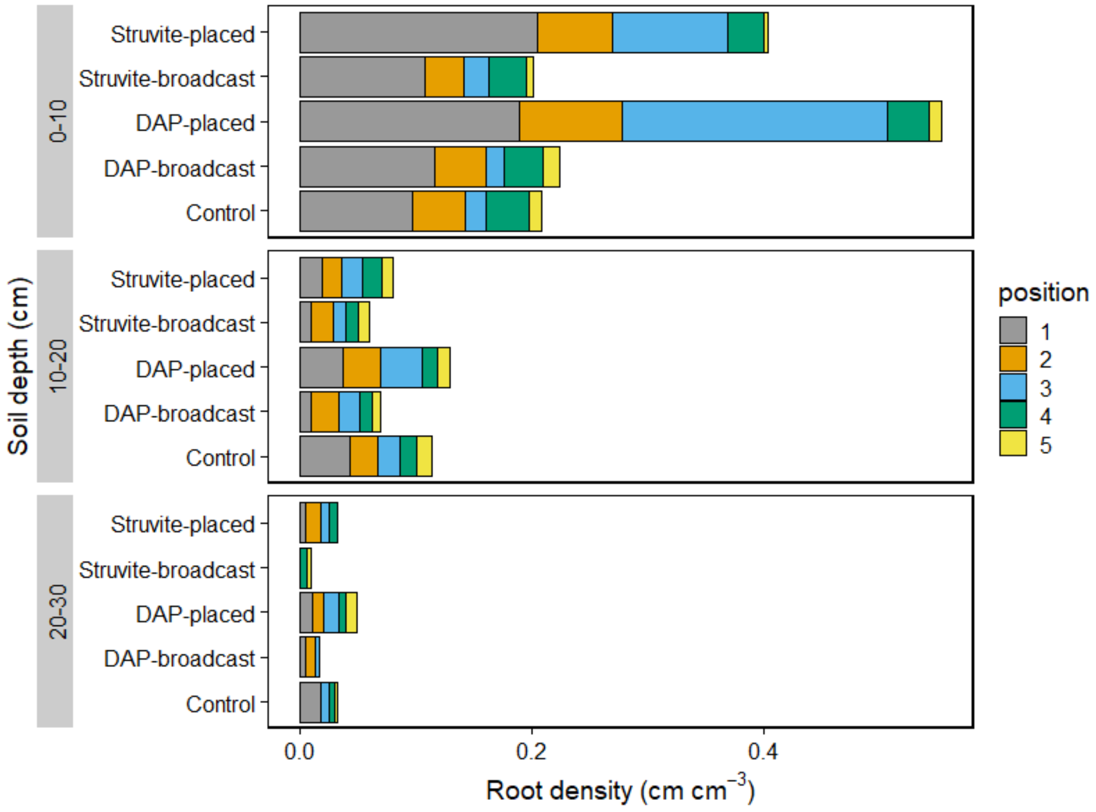


Figure 3. Distribution of maize root density (cm cm^{-3}) at 0-10, 10-20, and 20-30 cm soil depth and at 5 positions. Position 1: underneath the maize; position 2: in the middle of two adjacent maize plants; position 3: in the fertilizer band (placed) or equivalent reference position without fertilizer band (control and broadcast); position 4: opposite to the fertilizer band; position 5: in the middle of two maize rows.

4. Discussion

4.1 Placed struvite as a substitute for diammonium phosphate

The effect of the P fertilizer application method on bioavailability has been evaluated mostly for traditional mineral P fertilizers, which are water-soluble (Grant & Flaten, 2019; Nkebiwe et al., 2016). For mineral P fertilizers such as diammonium phosphate, localized application close to the seed can provide a high concentration of P to roots and also reduce the P immobilization in soil by minimizing the contact surface between the fertilizer and the soil, and by soil acidification of the rhizosphere following the uptake of the ammonium component through roots. In contrast to water-soluble mineral P fertilizers, struvite is nearly insoluble in water (Supplemental Table S3). The dissolution in the soil solution of P from granulated struvite was found to be much slower than from water-soluble mineral P fertilizers, and the diffusion of dissolved P from the granule may be limited (Degryse et al., 2017). Although maize has a large root morphological plasticity and can respond to a nutrient-rich zone (Gao et al., 2019), it is likely that in the broadcast treatment, young maize roots were not able to reach the dissolved P from struvite that was applied also between the rows, and growth was therefore impaired due to P limitation. In contrast, when placed close to the seed, the released P from the struvite granule is fully accessible for root uptake and to further improve the root proliferation in the P-rich zone.

This is supported by the finding of the high root density in the fertilizer row. At the 7-leaf stage, higher root density was found in the fertilizer row (position 3) than opposite to the fertilizer band (position 4) for struvite-placed (Figure 2), indicating a stronger root development at the struvite-concentrated area. A higher root density could also accelerate the dissolution of the struvite granule, as Ahmed et al (2016) showed using X-ray tomography, where the volume loss of struvite granules was correlated with the plant root density around the granule (Ahmed et al., 2016).

The low P use efficiency after broadcast application of struvite might provide an explanation for field studies where struvite had a low fertilizing effect on crops compared to the unfertilized control (Omidire, 2022; Wollmann & Möller, 2018). Nevertheless, the impact of other factors such as soil pH cannot be ruled out, as the soils in both field studies had higher pH than this study. A large soil P sorption capacity due to the high content of Al/Fe hydroxides could also cause a limited P fertilizing effect after fertilization. We conclude from our study that the application method can be a crucial factor when evaluating the fertilizer efficiency of struvite. Therefore, we recommend the placement of granulated struvite as P fertilizer in maize production in southern Germany.

4.2 Residual P fertilizing effect of struvite on triticale and faba bean

It was hypothesized that struvite P is less mobile in soil than P immediately released from water-soluble fertilizers because the struvite P release is extended over a longer period, which may coincide with the crop need closer than water-soluble P-fertilizers (Talboys et al., 2016). However, as demonstrated by the P offtake of triticale, the residual P from DAP and struvite had similar bioavailabilities in the soil, indicating that struvite has a similar P fixation rate in the soil as DAP after one cropping season. Wollmann and Möller (2018) reported no residual effect of struvite application in the second year of their study and suggested that struvite in soil undergoes the same transformation as mineral fertilizers from water-soluble P to less available P pools. In a three-year field study on the residual effect of different rates of struvite application, no significant differences were found among the application rates but among the year of the study, indicating that a fixed portion of P from struvite is available for crop independent of the application rate (Thiessen Martens et al., 2022). It was suggested that the P bioavailability of struvite was governed by soil processes rather than by crop demand. Unlike mineral P fertilizer, the interactions of struvite in soil and its by-product are less studied. A recent lab experiment (Qin et al., 2021) showed that calcium phosphates ($CaHPO_4$ or $Ca_3(PO_4)_2$) were formed on the surface of struvite during its dissolution in $CaCl_2$ solution (pH 6) where Ca concentration is in the range of the soil solution of arable soils (Blume et al., 2016). Hence, there might also be other limiting factors for the dissolution of struvite, such as precipitation on the struvite surface, under certain conditions. Faba bean is known to mobilize sparingly soluble P in soil via rhizosphere acidification (Zhou et al., 2009), which is in the favour of struvite dissolution. However, the result of this study did not show a higher P offtake of faba bean in struvite treatments than DAP treatments as expected. By observation, some of the struvite granules placed close to the root were still intact in the soil (Supplemental Figure S2) after maize harvest, because the lower water solubility of struvite enables a slow and limited dissolution of P around the fertilizer granule in such acidic soil (Degryse et al., 2017). Before the sowing of triticale and faba bean, soil tillage was conducted where the remaining struvite granules were incorporated into the soil and the distance between the residual struvite granule and the root was increased. Faba bean as a legume generally has less root plasticity in response to high P concentration in soils than cereals (Gao et al., 2019; Li et al., 2014) and therefore, the P from the residual struvite, which is relatively far from the root might have been inaccessible. A larger P offtake of faba bean from struvite may be possible if no-tillage is conducted and the plant row is established close to the initial fertilizer band zone. A field study with Alfafa showed an enhanced P use efficiency of placed struvite in the second year of the study, indicating its strong residual effect if no-tillage was performed (Thiessen Martens et al., 2022). Reduced tillage might be an alternative perspective for future studies on improving the residual P use efficiency of applied struvite.

4.3 Residual soil P after maize and subsequent crops

After crop P removal by maize and the subsequent crop, more than 80% of the fertilized P remained in the soil (Table 5). Based on the standard soil P test in Germany, at least struvite fertilization after the maize-faba bean cropping increased the soil available P to a higher level, where less P fertilization is needed for the crop in the following rotation (Wiesler et al., 2018). It may be attributed to the less crop P offtake in struvite treatments compared to DAP treatments.

Unlike water-soluble DAP, placed struvite was found partially undissolved after one crop season. The undissolved struvite granule in the soil could influence the result of soil P analysis if it is still intact by the time of sampling. Gu (2021) demonstrated the overestimation of 20-3900% on the soil P test values of struvite-fertilized soil due to the dissolution of residual struvite granules during the soil extraction, especially for tests using strongly acidic extractants. Thus, the time between struvite fertilization and soil sampling for the soil P test needs to be taken into consideration to avoid such overestimation of soil P status.

5. Conclusion

The result of the two-year field experiment shows the strong influence of fertilizer application method on the P use efficiency of struvite. This influence is likely due to the low water solubility and dissolution pattern of struvite granules in soil. Fertilizer placement is therefore recommended for struvite fertilization, which can achieve the same yield and P offtake of maize silage as placed DAP in a field with slightly acidic and low-P soil. The residual effect of placed struvite is also similar to that of DAP under these environmental conditions. Future research on the investigation and improvement of the P use efficiency of struvite in fields with different soil characteristics (e.g., pH and clay content) is needed for the broad practical use of struvite.

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Author contribution

Yawen You: Conceptualization; Investigation; Formal analysis; Methodology; Writing-original draft; Writing - review&editing. Tobias Hartmann: Conceptualization; Methodology; Resources; Supervision; Writing - review&editing. Peteh Mehdi Nkebiwe: Investigation; Supervision; Writing - review&editing. Torsten Müller: Conceptualization; Funding acquisition; Resources; Supervision; Writing – review&editing.

Conflict of interest

The authors declare no conflict of interest.

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Supplemental materials

Supplemental Figure S1. Photo of a plastic cylinder for root sampling.

Supplemental Table S1. Total yield, P concentration and P offtake of triticale in 2022.

	Yield	P concentration	P offtake
	Mg ha^{-1}	g kg^{-1}	kg ha^{-1}
Control	11.0	1.5	16.8
DAP-broadcast	12.3	1.4	17.6
DAP-placed	13.2	1.3	16.2
Struvite-broadcast	12.8	1.4	18.1
Struvite-placed	13.2	1.5	19.6
p-value (ANOVA)	0.4	0.06	0.8

Supplemental Table S2. Total yield, P concentration and P offtake of faba bean in 2022. The same letters in a column indicate no significant differences (Tukey’s test, $\alpha = 0.05$).

	Yield	P concentration	P offtake
	Mg ha^{-1}	g kg^{-1}	kg ha^{-1}
Control	7.6	1.9 b	15.0
DAP-broadcast	7.5	1.9 b	14.6
DAP-placed	9.5	2.7 a	25.1
Struvite-broadcast	8.3	2.1 ab	18.1
Struvite-placed	8.0	2.1 ab	17.1
p-value (ANOVA)	0.6	0.03	0.2

Supplemental Table S3. P solubility of struvite in water, neutral ammonium citrate, and citric acid (% of total P).

	Water	neutral ammonium citrate	citric acid
Struvite	4	65	97

Supplemental Figure S2. Photo of residual struvite granule in the soil after maize harvest in 2020.

6. Chapter IV

Sensitivity of three phosphate extraction methods to the application of phosphate species differing in immediate plant availability

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Article

Sensitivity of Three Phosphate Extraction Methods to the Application of Phosphate Species Differing in Immediate Plant Availability

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Abstract: Extractive tests for determining the plant-availability of soil phosphorus (P) give varying results due to the inherently different characteristics of the extraction solution. Generally, classical soil P tests such as the Olsen or calcium acetate/lactate (CAL) method do not give an indication on the total amount of plant available P, but merely give an indication of the equilibrium between soil and extraction solution. It is also not entirely clear which fractions of P are directly determined through the various methods of extraction, i.e., determined P must not be immediately plant available, as is the case for rock phosphate. It is therefore possible that extraction methods either over or under estimate the amount of P available for plant consumption. In this research, we compared three methods of soil P determination (CAL, Olsen and diffusive gradients in thin films (DGT)) with regards to their ability to determine P species ($Ca(H_2PO_4)_2$, $CaHPO_4$, $Ca_3(PO_4)_2$ and Inositol-6-hexakisphosphate) added to soils of high sorption capacity, immediately after as well as two weeks after application. For each of the methods, it could be shown that sorption processes in the soil immediately (0 days incubation) fix P to a point where it is not extractable through any of the described methods. These sorption processes continue over time, leading to a further decrease of determined P. The acidic CAL extraction method gives higher results of extractable P compared to the Olsen method. Due to the extraction of $Ca_3(PO_4)_2$, the CAL method may overestimate immediately plant-available P. The most suitable methods for the determination of immediately plant available P may therefore be the Olsen and DGT methods. Organic IP6 is not determined by any of the extraction methods. At low concentrations of soil P, the DGT method may fail to give results.

Keywords: diffusive gradients in thin films; phosphate availability; soil chemistry; plant nutrition; phosphate aging; phytate

1. Introduction

In recent years, attention has been brought to the depleting reserves of phosphate rock and the necessity of improving agronomic approaches to make the best use of available phosphorus (P) in agricultural soils, thereby reducing the need for frequent applications of P by farmers [1]. In order to improve agronomic practices that allow a reduction of P application to soil, it is necessary to relate P application to the P status of the soil, which can be determined through wet extraction of soils with acidic or alkaline extractants. In contrast to the rather straightforward method for analyzing the soil mineral nitrogen (N) status, the interpretation of results regarding available P is made difficult through the complex binding of P in natural soils [2,3].

In Europe, the extraction methods for the determination of soil P classification vary. In Germany and Austria, the main methods for extraction are the double-lactate method (DL) and the calcium-acetate-lactate method (CAL) [4,5]. As with other extraction methods, there is often confusion about the fraction of P determined by these methods, as the determined concentration of extracted P is related to "plant-available" P, even though the relatively aggressive, acidic extraction also releases P from sorbed and precipitated fractions that are not immediately plant available. Rather, the methods more likely describe an equilibrium between the soil and extracting solution, which is helpful only for classifying soils according to their respective P_{CAL} or P_{DL} concentrations in combination with long-term analyses of yield in dependency of soil P status. Even then, depending on soil-pH and other physical and chemical properties, the classification of soils may differ dramatically, leading to false assumptions on P availability of soils [6]. In some cases, soils classified as low in P_{CAL} nevertheless lead to high yields despite the omission of P application, while high P soils may respond to the application of mineral P.

In contrast to the acidic extraction methods, the Olsen method uses an alkaline extractant ($NaHCO_3$), thereby causing principally different desorption and dissolution processes in the soil-extractant mixture [3] and possibly causing a higher contribution of labile organic P fractions [6–8].

For basic purposes, such as the evaluation of soil P status as a guideline for P fertilization to agricultural systems, the method of extraction is suitable as long as the differences in P extraction from soil are taken into account [3]. Problems arise when the P status of the soil does not correlate to the observations of yield after P fertilization events, i.e., low P soils do not respond to P fertilization or high P soils respond to fertilization as mentioned above. In these cases, the extraction methods fail to give information on the underlying sorption and release processes. These observations, as well as recent developments of the global P market, have pointed out the need for suitable soil extraction methods that depict the availability of P in agricultural soils for plants, with the overall aim of increasing P use efficiency in crop production. As the classical extraction methods are not always reliable and must be evaluated according to their capacity for solubilizing bound, precipitated and sorbed P fractions, alternatives that better depict plant available P are being sought [9]. Further, it is necessary to identify analytical tools that allow sensitive observations of short-term changes to soil P fractions, thereby increasing our understanding of soil's physical and chemical processes determining P sorption and desorption [2].

Various analytical approaches, such as the Resin-P approach, using cationic absorption materials, and the diffusion method, using iron-oxide (FeO) impregnated filter papers [3,10], aim to imitate P uptake through plant roots, thereby determining both the soluble P fraction, as well as easily desorbed P fractions. A comparable approach is the diffusive gradients in thin films (DGT) method, which uses a ferrihydrite-containing hydrogel that allows the quantitative estimation of P concentrations in solutions/soil solutions by creating a concentration gradient of P near the DGT device [11–14].

In a recent paper, Christel et al. [14] described the sensitivity of the DGT method for the prediction of P availability in soils recently fertilized with pig slurry, stating that, while the capacity of the binding layer (ferrihydrite containing layer) of the DGT device was a limiting factor, the method could generally be used to depict increases in P availability after the application of organic fertilizers.

Yet it remains unclear which fractions of P are sensitive to DGT analysis and whether P extracted from agricultural soils is indeed only in the form of plant available P, or whether other, non- plant available fractions are extracted through the DGT method.

In this study, we determine the sensitivity of DGT devices and wet extraction methods (CAL and Olsen) in applications of different P species (calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$); calcium hydrogen phosphate ($CaHPO_4$); Tricalcium phosphate ($Ca_3(PO_4)_2$) and Inositol-6-hexakisphosphate (IP6)) to soils showing a high sorption capacity of P and an inherently low P_{CAL} fraction.

The aim of this paper is to determine which P fractions are sensitive to different extraction methods and whether or not CAL, Olsen and DGT are suitable methods for determining short-term changes in P availability driven by sorption/desorption processes of agricultural soils.

The hypotheses for this research were that (1) the determination of P from soils with recently added P forms depends on (a) the chemical characteristics of the extractant and (b) the water-solubility of the added P form and that (2) short-term changes of P availability in recently fertilized soils are best described through extraction methods that do not change the chemical equilibrium in soil/solution mixtures.

2. Materials and Methods

2.1. Test Soils

We collected soil from the uppermost 20 cm of two fields (Baimiskreuz, Hundsbrunnen) in the municipality of Hirrlingen, Baden-Württemberg, Germany (48°24′ N 8°53′ E). The soils were characterized by a relatively heavy texture and inherently low P_{CAL} and P_{Total} concentrations, for which they were primarily chosen, and differed in pH (Table 1), thereby making them suitable for principle investigations on P sorption after fertilization. In preparation of the experiment, the soils were air-dried and passed through a 5 mm mesh sieve. Soil pH was determined using the electrometric determination of H+ activity in a 0.01 M CaCl solution (1:2.5 soil (m) to solution (V)). Soil texture was analyzed through combined wet sieving (2 to 0.063 mm) and sedimentation (particles < 0.063 mm) after dispersion of soil samples and pre-treatment with H_2O_2 (pipette method according to Köhn) [5]. P_{CAL}, P_{Olsen} and P_{Total} were analyzed through standard procedures. All analyses were carried out according to VdLUFA standard methods [5].

Table 1. Important basic characteristics of experimental soils.

Field	pH	Sand (%)	Silt (%)	Clay (%)	Texture	P_{CAL} (mg kg^{-1})	P_{Olsen} (mg kg^{-1})	P_{Total} (mg kg^{-1})
Baimiskreuz	6.4	7	61	32	silty clay loam	16.5	11.6	510
Hundsbrunnen	7.4	5	66	29	silty clay loam	8.2	13.9	500

2.2. Experimental Treatments

In order to compare the sensitivity of 3 different P extraction methods, soil from the 2 fields described above was fertilized with 4 different P species, representing the primary ($Ca(H_2PO_4)_2$), secondary ($CaHPO_4$) and tertiary ($Ca_3(PO_4)_2$) calcium-salts of phosphoric acid (H_3PO_4) as well as an organic phosphate species, inositol hexakisphosphate (IP6). P was added at a dose of 100 mg kg (soil)$^{-1}$. An unfertilized control was included in the experimental design. With the two factors of soil and fertilization, the experiment comprised of 10 treatments with 4 laboratory replications each. The water content of the soil was adjusted to 18% (*w/w*). The soil was kept in glass jars at ambient temperatures for the duration of the incubation period (14 days). The soil was analyzed for P content using the CAL, Olsen and DGT methods at the beginning of the experiment (day 1) and at the end of the incubation period (day 14).

2.3. CAL Analysis

P was extracted from soil using CAL solution (0.05 M calcium-acetate, 0.05 M calcium lactate, 0.05 M acetic acid adjusted to pH 4.1) at 180 rpm for a duration of 90 min. As an adjustment to the original method, a measure of activated charcoal (1 tsp) was added to the soil and extractant solution before shaking to prevent the coloration of the extractant through humic substances in the soil. After shaking, the extract was filtered (150 mm MN 619 G filter paper) and prepared for the colorimetric determination (ammoniumvanadat/molybdat) of P concentrations at 436 nm wavelength.

2.4. Olsen Analyses

With the Olsen method, P is extracted from soil using a 0.5 M sodium bicarbonate ($NaHCO_3$) solution by shaking at 180 rpm for 30 min. The extractant was filtered (150 mm MN 619 G filter paper), after which P concentration of the extract was determined using inductively coupled plasma optical emission spectrometry (ICP-OES).

2.5. DGT in Standard Solution

DGT devices were deployed to solutions ranging from 1 to 100 mg (P) l^{-1} and an additional solution of purified water for 24 h at ambient room temperature (20 °C), after which the DGT devices were removed, rinsed with purified water and opened. Both the diffusive layer of the DGT device, as well as the ferrihydrite binding layer of the device were eluted separately in 4 mL 1 M HNO_3 for a period of 24 h, again at ambient room temperature. The P concentration of the eluant was analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

2.6. DGT Analysis in Soil

For the DGT analysis soil was prepared by creating a saturated paste of 50 g (soil) and 30 mL deionized H_2O. The saturation paste was left to settle for a period of 24 h, after which the ferrihydrite containing DGT devices (DGT Research, Lancaster, UK) were applied. After 24 h, the devices were removed and the ferrihydrite gel component of the DGT device was eluted in 4 mL 1 M HNO_3 for a further 24 h. The eluant was analyzed for P concentration using inductively coupled plasma mass spectrometry (ICP-MS). Data are displayed as P eluted per disc.

2.7. Statistical Analysis

The results were analyzed using the R environment for statistical computing [15] and the drc package for bioanalysis [16]. Data were analyzed for variance and differences between factors and their interactions were determined using the appropriate post-hoc test, as indicated in the results section.

3. Results and Discussion

3.1. DGT-Standard Curve

The uptake behavior of P from standard solutions ranging from 1 to 100 mg (P) l^{-1} corresponds with results previously described by Christel et al. [14] (Figure 1). The results of the standard curve indicate a sharp increase of P uptake into the binding-gel following a Michaelis-Menten curve with a calculated maximum uptake of 7.3 µg (P) $disc^{-1}$. The results indicate that the DGT method is sensitive to low concentrations of P and is a suitable method for determining the plant available fraction of P in agricultural soils.

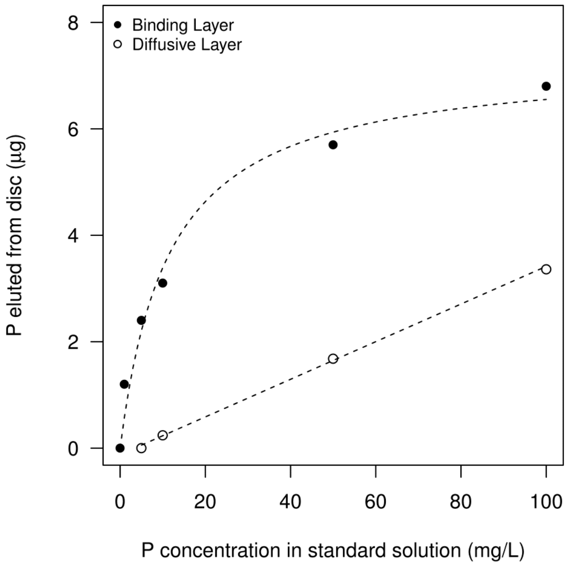

Figure 1. P eluted from a binding layer and a diffusive layer of diffusive gradients in thin films (DGT) devices following an exposure of 24 h to standard solutions with increasing phosphorus (P) concentrations and after the elution of the layers in 1 M HNO_3. The dotted lines indicate the Michaelis-Menten-like P uptake of the binding gel (with a calculated maximum capacity of 7.3 µg (P)) and the linear relation of the diffusion of P into the diffusive layer at increasing P concentrations.

3.2. Comparison of Extraction Methods

Due to negligible differences between the two soils, a two-factorial ANOVA was conducted for each soil separately, followed by Tukey's test for honestly significant difference (TukeyHSD) at a confidence level of $\alpha = 0.05$.

The results of our analysis show that, generally, the extraction methods used give highly contrasting results when trying to determine the availability of P for plant production systems. Differences in P determined through the extraction method follow a decreasing order of CAL > Olsen > DGT, which is consistent with results described by Wünscher et al. [3], even though the DGT method was not part of their investigation.

Of the P species used in our experiment, only $Ca(H_2PO_4)_2$ and $CaHPO_4$ may be considered to be immediately available for plant uptake, due to dissolution of the ions in soils. The remaining mineral P species, $Ca_3(PO_4)_2$ with its strong similarities to rock phosphate, as well as the organic molecule IP6 are not immediately available for plant uptake as chemical [17] and biological processes are needed to dissolve P over time [18,19]. Many of these processes may be plant-mediated. Regarding these basic observations of P availability for plants, the Olsen method returns the most understandable picture, as the P species is determined in a decreasing order $Ca(H_2PO_4)_2 > CaHPO_4 > Ca_3(PO_4)_2$ (Figure 2A,B). In contrast, the CAL method determines P species in a decreasing order of $CaHPO_4 > Ca(H_2PO_4)_2 > Ca_3(PO_4)_2$. The DGT method determines only the immediately available $Ca(H_2PO_4)_2$ and $CaHPO_4$ (Figure 2E,F).

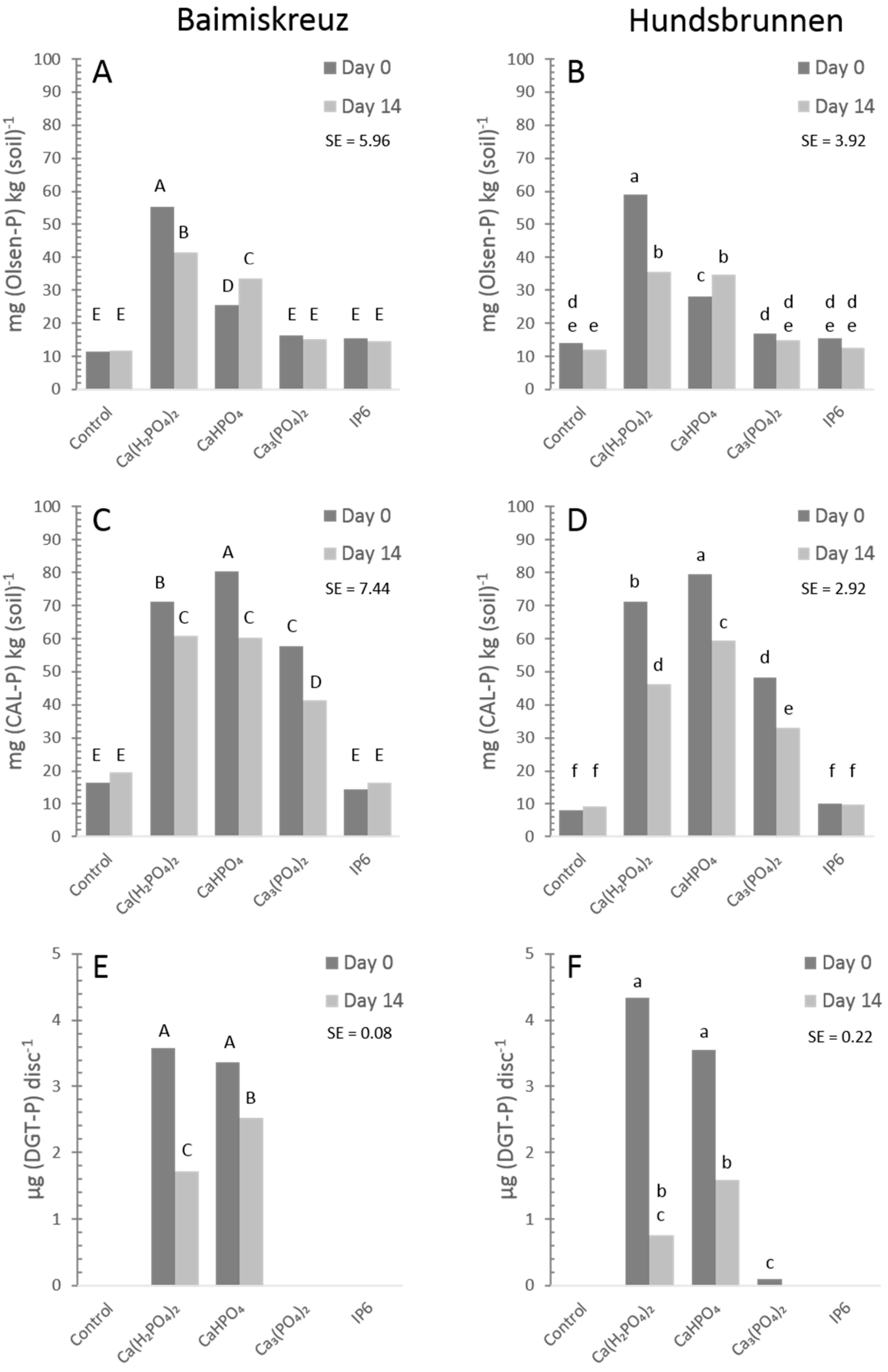

Figure 2. Olsen (**A**,**B**), calcium acetate/lactate (CAL) (**C**,**D**) and DGT (**E**,**F**) extracted P from the experimental soils Baimiskreuz (pH 6.4) (**A**,**C**,**E**) and Hundsbrunnen (pH 7.4) (**B**,**D**,**F**) after the addition of 100 mg (P) kg (soil)$^{-1}$. Where no bars are depicted, P concentrations were below the analytical detection limit. Letters above bars indicate significant differences between observations (P source × time, TukeyHSD, α = 0.05) evaluated for each soil separately, SE indicates the pooled standard error.

The results of our experiment further show that, irrespective of the extraction method, soil processes restrict the determination of added P immediately after application. The amount of P not extracted from soils increases after an incubation period of 14 days after application, except for the determination of $CaHPO_4$ through Olsen analysis, where P concentrations increase after incubation. Previous observations showed that, especially in low P soils, P sorption increases with the duration of incubation, especially at low rates of application [20,21].

The DGT method only determines P added through highly water-soluble P species. P species of higher molecular weight were not determined through the DGT method, thereby supporting the method as suitable for the determination of immediately plant available P.

As the acidic extraction of the CAL method may give false information on immediate P availability through the dissolution of unavailable $Ca_3(PO_4)_2$ species, only the DGT and Olsen method are suitable if immediate plant availability of P is to be determined. Of these two, only the Olsen method was able to determine changes to the immediately available P pool at low soil-P concentrations. Further, the Olsen method may be more reliable compared to the DGT method when the aim is to predict plant availability of P or when changes to the immediately plant-available P fraction are to be determined, as described by Burkitt et al. [22].

It has further been stated that, while the DGT method may accurately depict the amount of P immediately in solution, it may not always correlate well to plant performance as plant-mediated dissolution processes are not taken into account [23,24]. While the DGT method is described as an accurate method for the determination of plant-available P even at low concentrations in various soil types [9,25], our study only determined DGT available P after the addition of highly soluble P species, which may indicate the limits of the method when applied to soils that show both low P concentrations as well as a high sorption capacity, as indicated through the CAL and Olsen methods.

4. Conclusions

Our work identifies to what extent different P species are extracted from soils of high sorption capacity through common methods for the determination of P concentrations. It shows that processes of P sorption may lead to an immediate fixation of added P to a point where portions of added P are not determinable through extraction methods. When immediately plant available fractions and short-term changes of these fractions should be determined, researchers should choose extraction methods that only determine immediately plant available P forms (Olsen, DGT). Further, our research shows that, especially when the chemical equilibrium of soil/solution mixtures is changed through acidic extraction solutions an overestimation of plant available P is possible, especially when insoluble tricalciumphosphate-like P forms are present in the soil environment. Future research should focus on combined approaches to soil P analysis in order to identify the extracted P species, thereby allowing conclusions on soil chemical processes determining the plant availability of P in soils.

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7. General discussion

7.1 Opportunities and challenges of sewage sludge ashes as P fertilizer in agricultural production

The findings in chapter I and chapter II indicate that the direct use of untreated SSA as P fertilizer not only failed to promote plant growth and plant P offtake in the short term but also increased the risk of heavy metal accumulation in soils.

The thermal conversion of sludge includes incineration, gasification, and pyrolysis. They determine the P species in the ash and consequently its P bioavailability (*Thomsen* et al., 2017). In chapter I, the main crystalline P-compounds in the tested SSA is $Ca_3Mg_3(PO_4)_2$, which is not immediately soluble in water and available to plants. The treated SSA tested in chapter I was thermal-chemically processed together with Na-containing alkaline compounds to form P species similar to rhenaia phosphates. Other possible post-treatments of SSA either change the P compounds in the final product into a more soluble P species or extract the P using acid leaching (*Krüger* and *Adam*, 2015). Such post-treatment also aims to effectively lower the heavy metal content via chelating agents or physical separation (*Gorazda* et al., 2017; *Hermann* and *Schaaf*, 2019). The analysis of SSA in chapter II demonstrated the limitation of SSAs as P fertilizers or material for fertilizer production due to their high heavy metal concentration. A large share of heavy metal in SSAs comes from industrial sludge. 52% of SSAs in Germany are produced from a mixture of municipal and industrial sludge (*Krüger* and *Adam*, 2015), thus the separation of sludge before the thermal conversion is a possible solution to reduce the heavy metal concentration in SSAs.

The attempt of producing superphosphate with SSA in chapter II provided an alternative approach to reuse SSAs in fertilizer production. Our greenhouse study showed that a 25% substitution of rock phosphate by SSA to produce superphosphate at the lab scale can achieve the same fertilizer efficiency as the superphosphate produced with 100% of rock phosphate. The approach of using SSA in mineral P fertilizer production has the advantage of minimizing additional installations in incineration facilities and fertilizer factories. The upscaling of using SSA to produce superphosphate from lab-scale to pilot-scale was initiated by a company in 2019 (*ICL*, 2022), aiming at fully replacing rock phosphate in the fertilizer production.

Though limited in the short term, it is possible that the P availability of SSA increases over time under specific conditions. A greenhouse study using spring wheat found P solubilization of SSA over time in acidic soil, where the P uptake rate during 41-55 days of growth was 10 times higher than during 0-26 days of growth (*Mackay* et al., 2017). An early application time might be an appropriate way to enhance the P availability of SSA in acidic soils.

When brought from scientific research to practical use, the land application of SSAs and SSA-derived fertilizers should also be considered. The fine particle size could cause dust problems when broadcasting in the field, threatening human health and increasing the loss during application. Granulation of SSA is necessary to be safely and easily spread in the field. However, whether the alteration in particle size of SSA affects its P availability is less studied. The SSAs tested in experiments in pots and fields often have fine particle sizes and are mixed or incorporated into the soil (*Lemming* et al., 2017; *Mackay* et al., 2017; *Wollmann* et al., 2018), the same as the setup in chapter I and chapter II. As most of the SSAs (treated or untreated) have extremely low P solubility in water (*Kratz* et al., 2019), their dissolution in the soil is expected to be slower than water-soluble mineral P fertilizer. Based on the indication from the dissolution pattern of granulated and powdered struvite in soil (*Degryse* et al., 2017), it is likely that the larger particle size of granulated SSA leads to decreased P release compared to non-granulated SSA.

Nevertheless, SSAs show a substantial value in recycling and reusing P from wastewater to agriculture through advanced P recovery technologies. Issues like heavy metal contamination and land application are still needed to be tackled.

7.2 Opportunities and challenges of struvite as P fertilizer in agricultural production

Our studies demonstrated the high P use efficiency of struvite, which is comparable to mineral P fertilizer in pots and field studies. Such high efficiency, however, is obtained under certain circumstances. Factors like soil pH, the particle size of the fertilizer, and application method could influence the efficiency of struvite. Based on our findings in the field, it is recommended to replace mineral P fertilizer with granulated struvite using the fertilizer placement method in soil with slightly low pH. Other studies also investigated alternative ways to improve the efficiency of struvite, like using arbuscular mycorrhizae fungi (*Di Tomassi* et al., 2021), blending with other mineral P fertilizer (*Hertzberger* et al., 2021), and applying with ammonium-containing fertilizers (*Robles-Aguilar* et al., 2019). With increasing research focus on struvite, it may take up a share of the current P fertilizer market soon and together with other recycled P sources alleviate the dependency on P import in the EU.

The concern of contamination of struvite derived from sewage sludge cannot be neglected. Unlike SSA, the concentration of heavy metals in struvite is generally very low (*Muys* et al., 2021). The removal of heavy metals is also considered during the production process. For example, The Stuttgart Process uses citric acid in the solution phase of acidified sludge to bind metals as complexes (*Meyer* et al., 2019). The risk of microbiological contamination with struvite derived from sludge and food processing factories is also quite low and within the standard of the EU regulation (*Muys* et al., 2021). *Weissengruber* (2018) addressed the concern of persistent organic pollutants (POPs) residual in struvite and found minor risk with a 200-years accumulation using a simulated model. The struvite tested in our studies also has very low concentrations of a list of organic pollutants (S1), which are within the standard of sludge regulation and fertilizer regulation in Germany. There are also concerns about contamination of pharmaceutical residuals in struvite, but mainly for struvite derived from human urine. Studies found only minimal pharmaceutical residuals in urine-derived struvite produced with proper storage time and pH (*Kemacheevakul* et al., 2014; *Schürmann* et al., 2012; *Wei* et al., 2018), as most of the pharmaceuticals remain in the solution. Plant growth trials with urine-derived struvite also showed a minimal risk of pharmaceutical accumulation in tomatoes (*de Boer* et al., 2018). Compared to SSAs, the concentration of pollutants in struvite so far lies in the requirements of the EU regulation for fertilizing products. But the supervised product testing and continuous surveillance of the contaminants are imperative as the contaminant concentration in the sludge could also change with the seasons.

The high P use efficiency and low content of contaminants make struvite a suitable substitution for mineral P fertilizer. However, the P recovery rate of struvite production is in general lower than it of the SSAs (*Santos* et al., 2021), because SSA concentrates almost all P from the sludge. The precipitation process could recover 80-99% of P in the liquid phase of sludge after anaerobic digestion or in the liquid phase of acidified sludge (*Muys* et al., 2021), depending on the recovery technology. The ratio of P recovered in struvite and the total P in sludge or wastewater is often not clearly mentioned. *Tuszynska* (2021) found that 70-85% of total phosphorus in the feedstock was in the solid phase of digestate from sludge fermentation, indicating that the struvite precipitated from the liquid phase of digested sludge recovers only partial of the P in the wastewater. The Stuttgart Process, which produced the struvite tested in our studies, could recover a maximal 67% of total P in the digested sludge under certain conditions (*Meyer* et al., 2019). The P recovery rate (P in the final product / P in the input material) of various technologies has a wide range of 10-70% (*European Sustainable Phosphorus Platform* et al., 2023). The German sewage sludge ordinance requires at least 50% of P reduction in sludge for large wastewater treatment plants by the year of 2029 (*Bundesamt für Justiz*, 2017), urging the enhancement of P recovery rate in struvite production before its implementation.

7.3 Outlook and future research directions

There is a lot of progress made in recycling phosphorus from wastewater. On the technical level, many technologies have been developed and they are on their way to the highest technology readiness level. By 2023, 13 sewage P-recovery technologies operate or construct full-scale plants worldwide, with output products like P fertilizers and phosphoric acid (*European Sustainable Phosphorus Platform* et al., 2023).

Much effort has been made to promote the recognition of recycled P fertilizers from waste, like struvite and SSAs, as certified fertilizers in the EU market. On the 16th of July 2022, the revised regulation on EU fertilizing products came into force, which stated three categories of recycled fertilizer: precipitated phosphate salts and derivates, thermal oxidation materials and derivates, pyrolysis and gasification materials (*European Commission*, 2022). It is expected to have recycled P fertilizers on the market after the implementation by the member states.

One of many things that each member state needs to adapt to the new regulation is the fertilizer recommendation to farmers. As discussed above, SSAs (or SSA-derived fertilizer) and struvite have low P solubility in water, and the current fertilizer P test has difficulty predicting their P use efficiencies. As for land application, it is likely that the residual granulated recycled fertilizer remains in the field after one cropping season and interferes the corresponding fertilization recommendation for the subsequent crop based on the current soil P test. It would be a great challenge to formulate a proper guideline for recycled fertilizers and field studies on improving their efficiencies are required.

Life cycle assessment (LCA) of recycled fertilizers is also imperative to evaluate the environmental impacts associated with their products and applications. The LCA of two technologies that produced the fertilizers tested in this study, The Stuttgart Process (struvite) and AshDec© (treated SSA), showed that the former technology had a greater environmental impact than the reference system (wastewater treatment plant without recovering P technology) and the latter technology had a much less environmental impact (*Amann* et al., 2018). The high environmental impact of struvite production is due to its medium P recovery rate and intensive chemical use. Another LCA study also demonstrated the higher environmental impacts from the production and land application of recycled fertilizers derived from sludge in comparison to the triple superphosphate (TSP) (*Pradel* et al., 2020). It pointed out that the low P recovery rate, low fertilizer P content, and the large input of energy and reactants were the main contributors. Both LCA studies emphasized the importance of increasing the P recovery rate from sludge and minimizing the reactant inputs of P recovery technology. In addition, the system boundaries of LCA should also be considered when taking it into account during the decision-making. Nevertheless, much improvement of P recovery technologies from sludge is still needed regarding their environmental impacts.

So far there is no ‘perfect’ solution to the P recovery from wastewater in Germany. The recycled P fertilizers must obtain at least a similar P availability to plant as mineral P fertilizers, and their recovery technologies should have a recovery rate of at least 50%. According to the result of this study, both struvite and SSAs need improvements to meet the requirements. The most forward way might be to improve the P availability of SSAs, as they are currently largely produced in Germany. The long-term P effect of recycled fertilizers should be a future research focus. As discussed in Chapter I, the short-term P effect of SSAs is very limited. But its P solubilization in acidic soil over time could be a possible way to enhance its P availability. When the heavy metal concentrations in the SSAs are controlled below the maximum value, long-term field studies are necessary to investigate possible strategies for using SSAs as P fertilizers in agricultural production.

8. Conclusion

Two types of recycled P fertilizers from sewage sludge, SSAs and struvite, have shown great potential to replace phosphate rock-derived fertilizers in agricultural production. Untreated SSAs are not recommended due to the high heavy metal content and low P use efficiency, though the plant didn't uptake much heavy metal from the SSAs. Treated SSAs can achieve similar biomass of maize in the early stage, but their performances under field conditions still need to be tested. Struvite proved its high P use efficiency under greenhouse and field conditions, and the application method of fertilizer in the field has a significant impact on its efficiency. In our studies, the P availability of residual struvite was not obvious, as many factors influenced the result. Future research is needed to have a better understanding of residual struvite and the fertilization recommendation could be improved to adapt to insoluble recycled fertilizers.

With the development of the technology to recover more P from the waste and remove contaminants as much as possible, it is expected that recycled P fertilizer will take a bigger share of the fertilizer market in Europe.

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10. Supplementary information

S1. Concentrations of organic pollutants in struvite samples.

Organic pollutants	Maximal limit*	Concentration	Unit	Method
AOX	400	n.t. (<25)	mg kg^{-1} DM	DIN 38414-18:1989-11
Dioxins/Furans (WHO-TEQ)		3.4	ng kg^{-1} DM	AbfKlärV Anh. 1, 1.3.3.2:1992-05
dl-PCB (WHO-TEQ)		bdl (<<1)	ng kg^{-1} DM	AbfKlärV Anh. 1, 1.3.3.1:1992-05
Dioxins/Furans and dl-PCB (WHO-TEQ)	30	3.41	ng kg^{-1} DM	AbfKlärV Anh. 1, 1.3.3.1:1992-05
Perfluorooctanoic acid (PFOA)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Perfluorooctanesulfonic acid (PFOS)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Sum of PFOA and PFOS	0.1	n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Perfluorobutanoic acid (PFBA)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Perfluoropentanoic Acid (PFPeA)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Perfluorohexanoic acid (PFHxA)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Perfluoroheptanoic acid (PFHPA)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Perfluorononanoic acid (PFNA)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08

Perfluorodecanoic acid (PFDA)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Perfluorobutanesulfonic acid (PFBS)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08
Perfluorohexanesulfonic acid (PFHxS)		n.t. (<0.01)	mg kg^{-1} DM	DIN 38414-14:2011-08

[*] maximal limit in the German Fertilizer Ordinance

n.t: not detectable.

bdl: below detection limit

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