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Characterization of phosphate fertilizers recycled from biogas digestates and their influence on plant-soil fertility indicators

Dissertation

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„Neue Herausforderungen sind wunderbare Gelegenheiten, Neues über sich selbst zu erfahren."

Ernst Ferstl

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Abbreviations

AD	**A**naerobic **D**igestion
BioEcoSim	An innovative **bio-eco**nomy solution to valorize livestock manure into a range of stabilized **s**oil **i**mproving **m**aterials for environmental sustainability and economic benefit for European agriculture; European Commission grant No. 308637
CAL-P	**c**alcium-**a**cetate-**l**actate **p**hosphate (plant available P in soil)
DMY	**D**ry **m**atter **y**ield
GOBi	**G**anzheitliche **O**ptimierung der **Bi**ogasprozesskette zur Steigerung der betrieblichen, stofflichen, energetischen und ökologischen Effizienz unter besonderer Berücksichtigung der Produktion eines natürlichen kundenspezifischen Düngemittels, BMBF grant No. 03EK3525A
P	**P**hosphor, **P**hosphorus
Pi	**i**norganic **P**hosphor/**P**hosphorus
Po	**o**rganic **P**hosphor/**P**hosphorus
PR	**P**hosphate **R**ock
Struvite	magnesium ammonium phosphate
TSP	**T**riple **s**uper**p**hosphate

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1 General Introduction

1.1 Phosphorus in soil

1.1.1 Introduction

Phosphorus (P) was first discovered in 1669 by the German alchemist Hennig Brand, who heated the malodorous residues of urine with sand and coal and isolated white phosphorus (Weeks, 1933; Emsley, 2000), which was sold as medicine for a wide range of ailments (Jupp et al., 2021). Nowadays, we known that P, originated from collapsed supernovae in the universe, is an essential constituent to all known forms of life. Next to the elements C, O, H, N and S, P is the sixth most abundant element in living organisms and an essential building material for biomolecules. P is required for the formation of nucleotides in DNA and RNA molecules, for phospholipids in cell membranes and for NADP and ATP, the fundamental energy currency for many biological processes (Jupp et al., 2021).

Naturally, P is ubiquitous in soil and water in low concentrations as a consequence of natural erosion, with slow diffusion and high fixation to soil components (Shen et al., 2011). Within the natural P cycle, P is taken up by microbes, fungi and plants that are eaten by herbivorous and carnivorous animals. Animal waste and decomposition of plant and animal material return P to soil and water, where chemical and microbial degradation and mineralization of organic matter close the nutrient cycle. This P cycle was certainly not completely constant over time, but ebbs and flows were mainly balanced by the involved nature (Filippelli, 2008).

1.1.2 Inorganic and organic P in soil

P in soil exists in various chemical forms as inorganic P (Pi) and organic P (Po) (Shen et al., 2011). These forms differ in their properties and fate in soil (Hansen et al., 2004; Turner et al., 2007). Pi usually accounts for 35% to 70% of total P (Harrison, 1987) and consists primarily of P minerals like apatites, strengite, and variscite, and secondary P minerals like calcium (Ca) phosphates in alkaline soils and iron (Fe) or aluminum (Al) phosphates in acidic soils. Furthermore, Pi (anions) are adsorbed to soil constituents, such as sesquioxides, Al-silicates, Ca-carbonates, clay minerals and organic matter, through charge-related associations (Sanyal and De Datta, 1991; Richardson, 2001; Richardson et al., 2009). Pi in soil is usually stable and the slow release by weathering, desorption and dissolution makes Pi scarcely available to plants. Desorption and dissolution of Pi in soil is highly pH dependent. With increasing soil pH, solubility of Fe and Al phosphates increases, but solubility of Ca phosphates decreases (Hinsinger, 2001).

Organic P (Po) accounts for 30% to 65% of the total P in soil (Harrison, 1987). It mainly exists in stabilized forms as inositol phosphates and phosphonates, and active forms as orthophosphate diesters, labile orthophosphate monoesters, and organic polyphosphates (Turner et al., 2002; Condron et al., 2005). The Po can be released through mineralization processes mediated by soil microorganisms and plant roots.

1.1.3 P dynamics in the rhizosphere

In the rhizosphere, compounds like signaling molecules, inorganic and organic acids, mucilage (polar glycoproteins and exopolysaccharides) and enzymes are released to the soil, influence soil P availability and drive the conversion of Po compounds into Pi that can be taken up by plants (Richardson et al., 2005). These root-induced changes mainly involve proton release to acidify the rhizosphere, carboxylate exudation to mobilize scarcely available P by chelation, ligand exchange, and secretion of phosphatases or phytases (Neumann and Römheld, 2002; Zhang et al., 2010).

Phosphatase activity plays a fundamental role in the transformation of Po to Pi. They originate from different sources, namely plant roots, soil fungi, mycorrhizal fungi, and bacteria (Margalef et al., 2017). The activity of phosphatases is increased under P deficiency (Vance et al., 2003; Vance, 2008) and influenced by soil physical and chemical conditions like soil moisture, temperature, clay content, mineral composition, and soil pH (George et al., 2005). In acidic soils, acid phosphatases occur predominantly, whereas alkaline phosphatases prevail in alkaline soils (Tabatabai and Bremner, 1969; Eivazi and Tabatabai, 1976). Under P deficient conditions, the activity of extracellular acid and alkaline phosphatase in soil increases during plant growth (Tandano et al., 1993; Duff, 1994; Li et al., 1997).

1.1.4 Plant availability of P in soil

Although the total amount of P in soil can be high, its effective availability is low due to slow diffusion and high fixation in soils (Shen et al., 2011), caused by complex edaphic processes and interactions with soil components that in total contribute to a pool of residual P in soil (Bindraban et al., 2020). More than 80% of the P usually becomes immobile and unavailable for plant uptake because of adsorption, precipitation, or conversion to organic forms (Tsado, 2012). Overall, P can be a major limiting factor for plant growth, highly dependent on soil pH, mineral particles and soil microflora (Oelkers and Valsami-Jones, 2008).

The availability of P to plants is predominantly controlled by two key processes: the spatial extension of roots to effectively explore soil water, partly combined with mycorrhizal association (Richardson et al., 2009), and the rhizosphere chemical and biological processes such as the release of exudates from roots that increase soil P availability (Neumann and Römheld, 2002; Richardson et al., 2009; Shen et al., 2011).

Of all the different P forms present in soil, only orthophosphate (HPO_4^{2-} and $H_2PO_4^-$) can be taken up by plant roots (Shen et al., 2011). The form in which orthophosphate exists in solution changes with pH. Below pH 6.0, it is mostly present as $H_2PO_4^-$, and H_3PO_4 and HPO_4^{2-} are present only in minor proportions. The highest phosphate uptake rates were found at pH 6.5 for mineral soils and pH 5.5 for organic soils, where $H_2PO_4^-$ is the dominating form (Penn and Camberato, 2019). However, diffusion and mass flow of P ions from bulk soil to the rhizosphere is low (< 1mm over a few days, Hinsinger et al., 2005) and so high-affinity active transport systems against a steep chemical gradient across the plasma membrane are required for Pi uptake into root epidermal and cortical cells to meet plant requirements (Shen et al., 2011). Most of the P taken up by roots is loaded into the xylem and subsequently translocated into the shoot (Shen et al., 2011). Plants have specialized transporters at the root/soil interface for extraction of P from the soil water, as well as other mechanisms for transporting P across membranes between intracellular compartments, where the concentrations of Pi may be 1000-fold higher than in the external solution (Schachtman et al., 1998).

1.1.5 Plant adaptations for P supply

Plants display several physiological and morphological responses as an evolutionary adaptation to P deficit conditions in soil. Examples are an improved P acquisition and translocation efficacy, or internal recycling of stored P from old tissues (Shen et al., 2011). A specific case is mycorrhiza, a symbiosis of host-specific soil fungi and plant roots, where plants receive nutrients and water in exchange to assimilates (Richardson et al., 2009; Shen et al., 2011). Under P deficiency, plants have also developed root morphological and physiological adaptive strategies like the increase of the root/shoot ratio, root branching, root elongation, root topsoil foraging, and root hair growth. Some species can also develop cluster roots to mobilize and acquire P from the rhizosphere (Lynch and Brown, 2008; Vance, 2008). Generally, plant root geometry and morphology are important for maximizing P uptake, because root systems that have higher ratios of surface area to volume will more effectively explore a larger volume of soil (Lynch, 1995).

1.2 Phosphorus fertilization in agriculture

Next to nitrogen, P nutrition of plants is a key production factor for plant growth and development in agricultural crop production (Garg, 2008). P limitation can reduce crop yield and quality at all developmental stages, right from germination to maturity (Malhotra et al., 2018). With the use of mineral fertilizers in agriculture started only a century ago, the millions of years old natural P cycle began to be significantly changed. In order to secure crop yield for a fast-growing world population with rising demand for food, an intensification of agriculture and significant input of P to soil became necessary in most parts of the world (Withers et al., 2015; Nizami et al., 2017).

Phosphate Rock (PR) was discovered at the end of the 19th century as resource for P fertilizer production and replacement of the diminishing natural resource Guano. Since the introduction of high-yield crops in the 1960s (Green Revolution), the use of inorganic P mined from PR has steadily increased to 4.6 million tons per year in 1961 and further to approximately 21 million tons in 2015 (Yuan et al., 2018; Bindraban et al., 2020), which is 4 times more than the natural annual mobilization by weathering (Falkowski et al., 2000). An estimated global population growth to 9.7 billion people in 2050 (Wali et al., 2021) will, in consequence, keep the future global demand high to an estimated need of 22-27 million tons P per year (Mogollon et al., 2018; USGS, 2020).

PR as a finite global resource (Smil, 2000) decreases in global accessibility and purity (Schröder et al., 2011) and is unequally distributed around the globe. About 70 % of the confirmed reserves of P ore are located in Morocco (Western Sahara), China and USA (Schoumans, 2015; De Ridder et al., 2012). This asymmetric distribution, together with its vast use in global agriculture and a lack of technical alternatives gives rise to economic, social, and environmental imbalances (Cordell and White, 2009; Cooper and Carliell-Marquet, 2013). Aside from unconfirmed reports of P ore findings in Norway (Bushuev, 2021), Europe almost entirely depends on PR imports and its associated price volatility (e.g. eightfold price increase in 2008, Jupp et al., 2021).

Only a small fraction of P supplied to soil as fertilizer is actually taken up by plants. A large proportion of P is either bound to soil components leading to accumulation, or washed out into surface and groundwater via leaching, runoff, and/or erosion. In both cases, either indirectly after soil saturation, or directly by solution into soil water, the excess of P in agricultural soils ultimately leads to a disperse distribution into the environment. In freshwater and marine ecosystems, the dispersion of P often causes eutrophication (Conijn et al., 2018), and ultimately a reduction of biodiversity (Wang et al., 2019).

The increasing demand of P fertilizers in agricultural production, together with the limits of PR as a P resource, the associated diffusion of P into the environment and the negative environmental side effects of its non-circular use, make it necessary to develop technologies for efficient P recovery and recycling for a more sustainable and circular use, that can ultimately replace significant portions of PR as geological resource.

1.3 Circular economy in agriculture

A circular economy in agriculture describes a production process where application and recovery should be closed in a loop to prevent loss and dissipation of nutrients into the environment where these often become pollutants (Scholtz, 2017). The idea of circularity includes the use of by-products from one production process as secondary raw materials in another (Hansen, 2018).

Important elements of a successful recycling are:

(1) a recycling technology optimized for high yield, low waste, low material and energy input and low hazard potential
(2) a complete chemical and physical characterization of the recycled material and finally a specification for a defined quality of the resulting products
(3) detailed knowledge of the product efficiency in different use situations
(4) a reliable and reproducible mixing and application technology tailored to the use situation.

Finally, the establishment of a total material and energy balance, taking into account possible side effects, is essential to quantify the efficiency of the recycling process (Shen et al., 2011). Input would include any production, transport, and application – related effort for crop fertilizers. And output would balance the entire nutrient removal from the soil by crop uptake and harvest, runoff, erosion, and leaching, as well as energy production and associated side effects.

1.4 Phosphorus recycling from anthropogenic use

Agriculture accounts for the worldwide consumption of ca. 80% of P from PR as fertilizer (Zapata and Roy, 2004). The use of P is still inefficient, mostly non-circular and highly dissipative, and due to losses during use, only 10% of P applied in global agriculture reaches the (human) consumer (Ott and Rechberger, 2012).

Van Dijk et al. (2016) gave an overview of the anthropogenic P-streams in Europe based on data from 2005. Of an overall import of 2390 Gg P, half of that amount (924 Gg) accumulated in agricultural soils and half (1217 Gg) was lost to waste from human consumption (655 Gg), food processing (339 Gg), animal production (62 Gg) and non-food production (77 Gg). Losses from human consumption were mostly wastewater (55%), food waste (27%) and pet excreta (11%). The largest reciprocal P material flow was recorded between crop production (mostly animal feed: 1460 Gg) and animal production (mostly manure: 1749 Gg).

The EU has identified P recycling as an essential political goal and expects an up to 30% replacement of the inorganic fertilizers by bio-waste in the next future (Hansen, 2018). The "green deal" initiative of the EU Commission to limit global climate change to two degrees Celsius by changing the European energy policy, encourages sustainable, cyclic economy to climate-neutrality by 2050 (European Commission, 2019). The regulatory framework effecting nutrient recycling in the European Union is summarized by Kabbe et al. (2017) and comprises of the water framework directive (WFD – 2000/60/EC), the urban waste water directive (91/271/EEC), the sewage sludge directive (86/278/EEC), the waste framework directive (2008/98/EC), the nitrate directive (91/676/EEC, the industrial emissions directive (2010/75/EU), the animal by-products regulation (2009/1069/EC) and the REACH guideline (2006/1907/EG).

Specific for fertilizers, the most recent update of the fertilizer product regulation 2019/1009 lays down rules for the quality, labelling and market placement of fertilizer products with special reference to phosphorus recycling. The fertilizers regulation was first in the EU's circular economy package that listed P as critical raw material (Grohol et al., 2018). This and the following legislations caused an increasing interest in the development of technologies for P recovery from wastewater and other renewable sources. The new EU fertilizer production regulation introduces product function categories (PFC) regarding materials to be used as fertilizers, and component material categories (CMC) which encompass raw materials for fertilizer production. The latter is now expanded to digestates, composts, animal by-products, struvite, biochar, sewage sludge and its derivative ashes. When defined quality requirements are fulfilled, outputs have product status and are no longer considered waste, removing legal hurdles, and promoting marketing for these materials. Another important change was the introduction of a Cadmium (Cd) limit on fertilizers. A maximum of 60 mg Cd per kilogram P_2O_5 dry matter (a calculated reference for total P in fertilizers) is now mandatory (Jupp et al., 2021).

An overview over a range of different chemical and thermal P recycling technologies from a variety of human resources has been published by Chojnacka et al. (2020); Jupp et al. (2021) and Egle et al. (2015). Amongst these, biogas plant digestates have become an increasingly attractive resource for P recovery. In most cases, biogas production uses a combination of livestock manure and energy crops under anaerobic conditions (Schoumans et al., 2015; Vaneeckhaute et al., 2018), resulting in digestate as waste. The recycling of biogas digestates to defined fertilizer products represents an attractive possibility to reduce external inputs and close the nutrient cycle, and thus has been subject of research in recent years.

1.5 P recycling from biogas plant digestates

Anaerobic digestion (AD) is the most widely used and mature technology for the production of biogas. In Europe, biogas is mainly produced from fermentation of energy crops, manure, and agricultural waste (Scarlat et al., 2018). In 2019, more than 18,943 biogas plants were counted in Europe (EBA, 2020). With the German Renewable Energy Act that first came into force in 2000, the establishment of biogas plants was encouraged in the country and nowadays more than 10,971 agricultural biogas plants are operating, especially in regions with high livestock density (EBA, 2018).

AD is carried out by microorganisms associated in a complex community in a closed system under controlled environmental conditions. In the absence of oxygen, the amount of organic matter in the substrate is significantly reduced (>50%) by conversion into methane (Tambone et al., 2009). The remaining digestate contains high amounts of plant nutrients (N, P, K) and residual organic matter and has therefore be used directly as soil fertilizer (Möller and Müller, 2012). Nutrients in these digestates are apparently more accessible to plants than those in the raw material (manure). The alkaline pH of unprocessed biogas digestates contributes to a reduction of soil acidification and its high fertilizing potential in comparison to mineral fertilizers has been confirmed in several studies (Formowitz and Fritz, 2010; Gunnarsson et al., 2010; Walsh et al., 2012; Möller and Müller, 2012).

The use of AD is generally critical in regions where a large amount of organic waste is produced (e.g. in regions with high livestock density), because the soil application of digestate or any other crop fertilizer is only allowed in the growing season. At times of the year when there is little plant uptake (autumn and winter), nutrient loss (especially N and P) into ground and surface water has to be avoided, and fertilization is therefore restricted by local or governmental regulations (e.g. the German "Düngemittelverordnung", DüV, 2017, last amended 2021).

Biogas stations in Germany alone (mean values of the years 2007 and 2008) produced 65.5 million cubic meters of digestate per year containing a total amount of 74.075 Mg P, 390.153 Mg N and 331.472 Mg K. Transport and storage of digestates and its derived nutrients is therefore necessary to avoid environmental problems related to nutrient overdoses. While biogas can be used directly as renewable energy source, the digestate, a mixture of degraded organic matter, inorganic nutrients and water, can be further processed for volume reduction and quality enhancement to produce transportable and storable fertilizer fractions (Hjorth et al., 2010).

Different technologies for nutrient concentration and volume reduction, based on physical and chemical processes are known today and the main technologies were published by Fuchs and Drosg (2013); Drosg et al. (2015); Campos et al. (2019); Bindraban et al. (2020) and Jupp et al. (2021).

A common practice for the separation of solids and liquids is the use of screw press separators. Möller and Müller (2012) summarized several solid and liquid characterization results by different authors in their review: the solid fraction often comprises approximately 25% and the liquid fraction around 75% of the total digestate fresh matter. The resulting liquid fraction of digestate after separation has a DM content of around 5% and typically contains high amounts of N (around 9% DM) with 40-80% of the total N being ammonia N (NH_4^+). Total P represents around 0.5% DM, K approx. 4% DM and total C 48% DM. The solid fraction of digestates has a DM content of around 24% and is characterized by total N of approx. 3% DM, whereof 40% is ammonia N. Total P represents 2% DM, K around 4% DM and total C around 40% DM.

From the liquid phase, a widely used recovery technology for N and P is the chemical precipitation by the addition of $Mg(OH)_2$ under alkaline conditions to form struvite ($MgNH_4PO_4*6H_2O$, ammonium-magnesium-phosphate). Struvite has been shown to be an effective slow-release P fertilizer under a wide range of soil pH conditions for agriculture and horticulture (Cabeza et al., 2011; Talboys et al., 2016). Several publications summarize and compare different technical approaches to recycle P from various sources into applicable fertilizers (Römer and Steingrobe, 2018; Cabeza et al., 2011; Lekfeldt et al., 2016).

The common practice for the separated solid digestate, also to improve the economically feasible transport costs, is drying, followed by pelleting or composting (Maurer et al., 2010; Meissl et al., 2007, Teglia, 2011). Both treatment procedures, however, cause significant N losses into the air as NH_3 (Maurer, et al., 2010; Rotz, 2004). Therefore, it was recommended that the separated solid digestate should be applied to the field as soon as possible (Möller and Müller, 2012) or that the drying process should be conducted under controlled conditions with subsequent N recovery or ammonia removal before or after solid-liquid separation (Möller, 2015).

A new, alternative recycling process specifically for digestate fractions of biogas plants was developed by Bilbao et al. (2015). The experimental work of this thesis was centered around the agronomical characterization and applicability of the fertilizer fractions obtained by this method, in comparison to conventional P fertilizers widely used in agriculture. The process is described below.

1.6 The P recycling process of the GOBi project

Within the BMBF funded research project GOBi (General optimization of the Biogas Process chain, grant No. 03EK3525A) a recycling process for biogas digestates was developed and patented in 2015 by the Fraunhofer IGB, Stuttgart, Germany. The recycling process was found to be a robust technology for use at pilot to production scale for the recycling of nutrients and an upgrade of digestates to storable and transportable products. A process overview is shown in table 1, where the recycling products are labelled as blue boxes. The three derived fractions investigated in this thesis were (1) P-Salt, recovered from the liquid fraction by precipitation, and (2, 3) two solid fractions, recovered from the remaining material by different drying techniques.

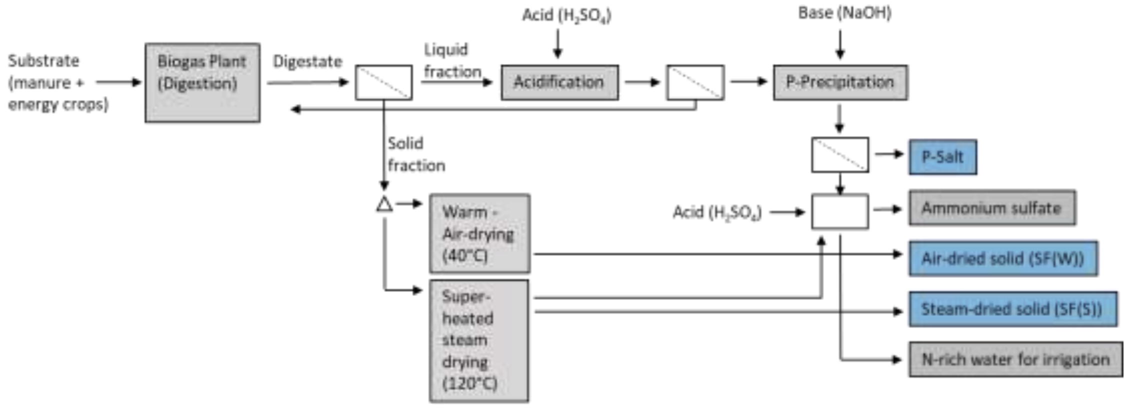

Figure 1: Recycling process of biogas digestates by Fraunhofer IGB, Stuttgart. Patent Classification C01B25/45. (Bilbao et al., 2015)

In a first step, the digestate was acidified, so that a maximum of P completely dissolved in the water. After that, a mechanical filtration was performed to separate solids from the liquid fraction. The solid fraction was dried with a warm air dryer or alternatively with a superheated steam dryer.

The P from the liquid fraction was recovered by alkaline precipitation and filtered off as a mixture of calcium phosphate, magnesium phosphate and struvite.

As a practical example, 1219 kg digestate (containing 9-11 mass % DM) was separated into a liquid fraction (1000 kg, 6 mass % DM) and a solid fraction (219 kg, 20-30 mass % DM). The drying process of the solid fraction (by warm air or hot steam air) resulted in 83,4 kg dried solids (named SF(W) or SF(S) for use as fertilizer. From the liquid fraction (1000 kg) subjected to precipitation, an amount of 7,1 kg P Salt was isolated (80 mass % DM), dried and milled to a fine powder (P-Salt) for use as fertilizer. Further to P, ammonium was precipitated from the liquid fraction with sulfuric acid to form ammonium sulfate (21.5 kg), that was again isolated, dried, and milled for use as fertilizer. The salt-depleted remaining liquid fraction (1188 kg) was finally made available for irrigation.

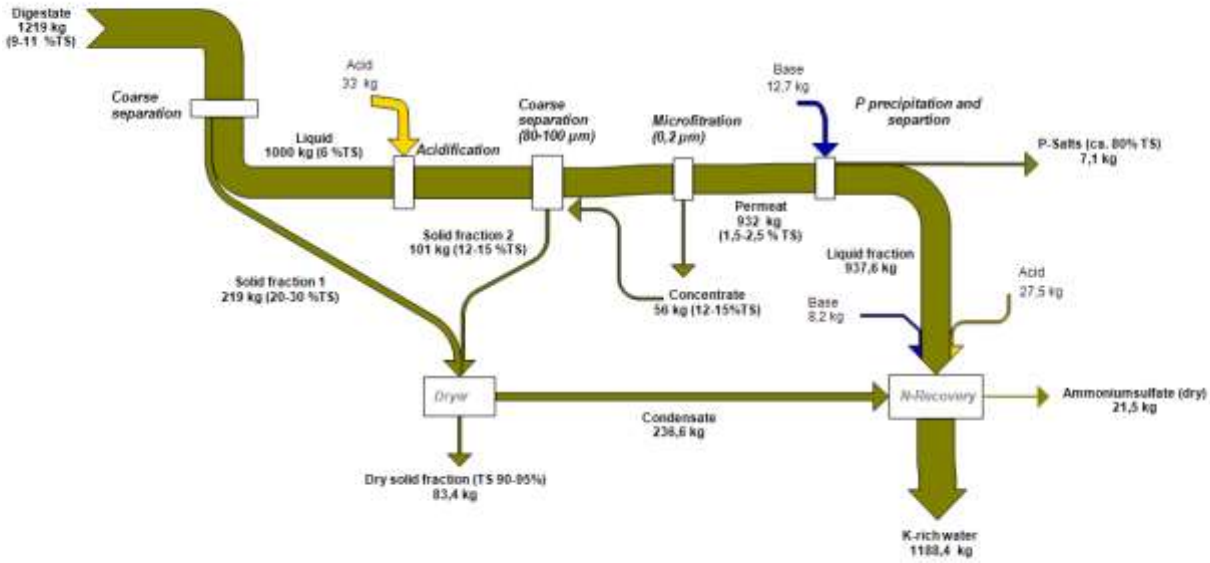

Figure 2: A mass balance example of the digestate recycling process by Fraunhofer IGB (source: Fraunhofer IGB, 2015)

1.7 Aims and objectives

Within the BMBF research project “General Optimization of the Biogas-process- chain” (GOBi), different recycled P fertilizers from a biogas plant were investigated for their suitability as alternative P fertilizers, compared to triple superphosphate (TSP) as reference. Aspects investigated were the P fertilization efficiency on different crops and different soils, P uptake into plants and effects of different fertilizer mixtures. P fertilization efficiency is defined as the crop yield per unit fertilized P.

The objectives of this research were:

(1) to assess the potential use of fractions produced from digestate of a biogas plant (by precipitation and drying) for their P fertilization performance in comparison to unfertilized controls and to a reference mineral P fertilizer, in different plants and different soils

(2) to evaluate combined application and different dosing techniques for their fertilization performance

(3) to assess P uptake of recycled fertilizers in comparison to the reference mineral fertilizer in different soils and plants

(4) to evaluate differences between recycled fertilizers from biogas production using pig manure vs cow manure

The following main hypotheses were evaluated:

(H_1) P-Salt, prepared from biogas digestates or manure by the Fraunhofer IGB recycling process, has a P fertilization efficiency similar or superior to triple superphosphate (TSP).

(H_2) The dried solids of the recycling process have P fertilizing and soil conditioning effects.

(H_3) The fertilization effects of P-Salt and solids in combination can be synergistic or additive.

(H_4) The drying method for the recycled solids influences their P fertilization efficiency.

(H_5) Soil fertilization efficiency of the recycled products is affected by soil pH and soil type in a similar way than TSP.

(H_6) The plant uptake of phosphate from soil fertilized with recycled P fertilizer fractions is comparable to TSP.

(H_7) Biomass increase after P fertilization of different plant species is similar between TSP and recycled fertilizers.

(H_8) CAL-P, the indicator for plant available P in soil, is increased by recycled P fertilizers to the same extent as TSP.

1.8 Structure of the thesis

Apart from the General Introduction and Discussion, this thesis includes four chapters that attend to the aims and objectives stated above. These chapters comprise three original research manuscripts published in international peer-reviews journals (Chapter 2, 3, 4) as well as one original research paper submitted for publication (chapter 5).

Chapter 2: **Can Phosphate Salts Recovered from Manure Replace Conventional Phosphate Fertilizer?** Ehmann, A.; Bach, I.-M.; Laopeamthong, S.; Bilbao, J.; Lewandowski, I. (2017). Reprinted from Agriculture, 7, 1.

Chapter 3: **Phosphates recycled from semi-liquid manure and digestate are suitable alternative fertilizers for ornamentals.** Ehmann, A.; Bach, I.-M.; Bilbao, J.; Lewandowski, I.; Müller, T. (2019). Reprinted from Scientia Horticulturae 243, 440-450. Ehmann and Bach share the first authorship.

Chapter 4: **Efficiency of Recycled Biogas Digestates as Phosphorus Fertilizers for Maize**. Bach, I.-M.; Essich, L.; Müller, T. (2021). Reprinted from Agriculture, 11, 553.

Chapter 5: **Efficiency of Phosphorus Fertilizers Derived from Recycled Biogas Digestate as Applied to Maize and Ryegrass in Soils with Different pH**. Bach, I.-M.; Essich, L.; Bauerle, A.; Müller, T. (2022). Reprinted from Agriculture, 12, 325.

2 Can Phosphate Salts Recovered from Manure Replace Conventional Phosphate Fertilizer?

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Article

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Abstract: Pig farming produces more manure than can reasonably be spread onto surrounding fields, particularly in regions with high livestock densities and limited land availability. Nutrient recycling offers an attractive solution for dealing with manure excesses and is one main objective of the European commission-funded project "BioEcoSIM". Phosphate salts ("P-Salt") were recovered from the separated liquid manure fraction. The solid fraction was dried and carbonized to biochar. This study compared the fertilizing performance of P-Salt and conventional phosphate fertilizer and determined whether additional biochar application further increased biomass yields. The fertilizers and biochar were tested in pot experiments with spring barley and faba beans using two nutrient-poor soils. The crops were fertilized with P-Salt at three levels and biochar in two concentrations. Biomass yield was determined after six weeks. Plant and soil samples were analysed for nitrogen, phosphorus and potassium contents. The P-Salt had similar or even better effects than mineral fertilizer on growth in both crops and soils. Slow release of nutrients can prevent leaching, rendering P-Salt a particularly suitable fertilizer for light sandy soils. Biochar can enhance its fertilizing effect, but the underlying mechanisms need further investigation. These novel products are concluded to be promising candidates for efficient fertilization strategies.

Keywords: manure; phosphorus recovery; struvite; biochar; spring barley; faba bean

1. Introduction

European agriculture is currently facing the problem of the accumulation of large amounts of slurry and manure, particularly in regions with high livestock densities, for example northwest Germany, Flanders and the Netherlands. Slurry and manure contain considerable amounts of important plant nutrients, including phosphorus (P) and nitrogen (N). It has been estimated that if the Netherlands applied its manure up to the allowed amount of phosphate on all its agricultural land, in 2015 there would have still been excess manure containing 40–60 million kg of phosphate [1]. Dealing with these manure and nutrient excesses is becoming an increasingly urgent challenge, and is heightened by the trend towards larger farm sizes as a consequence of increasing economic pressure. Manure storage is not only cost-intensive but is also associated with nutrient losses [2], leading to environmental problems such as air pollution (gaseous N emissions in the form of ammonia and nitrous oxide) and groundwater contamination (nitrate leaching).

Today, large livestock producers often buy a substantial proportion of their animal feed instead of growing it on their own farm. Most protein feed used in Europe, for example, is soybean meal, which has to be imported from South America. Farmers are no longer limited by regional feed supply and availability of arable land. Nutrients are imported along with the feed and remain in surplus on the farm within the manure. The livestock farms have too small a land area for the environmentally friendly field application of the accumulating nutrient load without exceeding the legal limits set by the European Union (EU) Nitrates Directive [3] and the EU Water Framework Directive [4]. Consequently, manure is considered a waste rather than a valuable resource. The situation is aggravated by the lack of regionally available, environmentally sound manure treatment solutions and the high costs of storage and disposal. As an example, Dutch farmers pay between €5 and €20 per tonne for the transport of surplus manure to other locations within the Netherlands [5] or even abroad.

By contrast, in other regions nutrients are needed—for example, at sites where arable farming is predominant and animal feed is produced for export. However, the high water content (>90%, [6]) makes long-distance transportation of manure neither profitable nor ecological. As a consequence, soil organic matter contents are depleted at these sites and nutrient deficits replaced through synthetic (N) or mineral (P, and potassium, K) fertilizers [7], which considerably interferes with the global P cycle [8].

Synthetic N fertilizers are mainly produced through the Haber–Bosch process. This process uses N from the air (thus unlimited in availability), but also consumes high amounts of natural gas and energy [9]. In contrast, mineral fertilizers are mainly derived from fossil resources and are, as such, limited. This is especially true for fossil P sources.

As a vital component of DNA and ATP, P is essential for all living organisms. Thus, it is one of the main nutrients needed for crop nutrition. The goal of achieving food security for a growing world population, the increasing use of biomass for biofuel production and the progressive degradation of arable land have all led to P fertilizer becoming more important for agricultural production than ever before.

In 2013/14, annual phosphate fertilizer consumption in Germany was 284,000 t [10]. In 2011, total EU phosphate consumption (fertilizer and industrial use) stood at approx. 4.6 million t per year. This represents 10% of global phosphate demand [11].

Phosphate fertilizer used in agriculture is mainly produced from rock phosphate (RP). However, RP is a finite resource, as with all mined resources. For this reason, in 2014, the EC added it to the list of critical raw materials [11]. Contrary to assertions in previous studies, there are still sufficient supplies of RP, but its extraction is very complex and not (yet) economically viable [12]. In addition, mined RP is increasingly contaminated by uranium and cadmium [13]. As 82% of the phosphorus extracted is used for fertilizers, these pollutants end up in the environment [11].

For this reason, prudent management of available P resources is of paramount importance. Exploiting "fresh" RP resources is one option. Another is the recycling of already "exploited" P, for example from livestock manure.

Livestock manure contains highly plant-available forms of P (inorganic) and N (ammonium) [14]. As such, it is a valuable organic fertilizer and a promising resource for P and N recovery. The manure excreted in EU-27 every year contains 1.8 million t of P, which corresponds to 150% of the amount of P used annually in fertilizers in Europe [2]. Thus, P recovery from manure could theoretically more than meet the entire demand for P fertilizer in Europe—providing the fertilizing effect of the recovered product is comparable.

The EC-funded research project "BioEcoSIM" ("An innovative bio-economy solution to valorise livestock manure into a range of stabilised soil improving materials for environmental sustainability and economic benefit for European agriculture"; grant No. 308637) has succeeded in developing an innovative technology at pilot-scale to recover P and N from pig manure. In a first step, manure is pretreated, so that the P completely dissolves. Subsequently, the manure is separated into a solid and a liquid fraction. The solid fraction is dried and then pyrolyzed to biochar. The P is recovered from the liquid fraction by precipitation and filtered off as a mixture of calcium phosphate (hydroxyapatite), magnesium phosphate and magnesium ammonium phosphate (MAP, struvite). The raw manure contains sufficient magnesium (1.7% dry matter) to allow struvite formation; no additional magnesium source is necessary. In this study, the obtained product is referred to as phosphate salts or "P-Salt".

This innovative technology has several advantages. It contributes to an environmentally friendly solution to the problem of manure disposal. It addresses the unfavourable nutrient ratio of manure, which often leads to an oversupply of P, as the amount of manure used in fertilization is usually calculated based solely on its N content. This also avoids the accompanying negative environmental consequences, such as P accumulation in soil, surface runoff and eutrophication of waterbodies. As the nutrients P and N are recovered separately, they can be used to create customized fertilizers as transportable and marketable products. This allows the fertilization of crops according to their respective requirements and the balancing of disrupted nutrient cycles. The technology could also reduce the EU's dependency on P imports. The improvement in P-use efficiency could help to conserve fossil P resources and reduce energy consumption in mining.

Struvite has been shown to be a highly effective, slow-releasing P fertilizer [15,16]. Several studies have found that struvite recovered from different materials can improve the yields of various crops compared to untreated controls [17–19]. Struvite recovered from swine wastewater has been shown to increase the biomass yield of maize more than commercial P fertilizer [20].

However, the plant availability of P in recovered products is often low, or at least unpredictable [21]. The assessment of fertilizers based on analytical results alone is not sufficient, because the predicted and actual availability and uptake of P by plants can differ substantially. Johnston and Richards [22] as well as Römer [23] confirmed that some P fertilizers ensure relatively good P availability and supply despite the small amounts contained in water-soluble form. Cabeza et al. [17] concluded that the dissolution of P in soil is a much more accurate indicator of the fertilizing effectiveness of recycled P products than their solubility in water or citric acid. Thus, plant experiments are crucial to evaluate the actual efficacy of the P-Salt in terms of P-fertilizing performance.

Biochar is produced from the solid manure fraction in the BioEcoSIM process and can serve as a potential soil improver. Biochar made from different substrates was reported to have beneficial effects on crop yield, soil quality and soil biological activity [24]. It can be used as an amendment to increase the water and nutrient retention capacity of light soils [25,26], thus aiding the sustainable production of food, feed and energy crops on progressively degrading soils—one measure to help meet the demand of an increasing world population. It also functioned as a means of carbon sequestration in soil [27,28] and has been shown to contribute to the mitigation of greenhouse gas emissions [29,30]. However, the use of biochar as a soil-improving substance is controversial and some studies have found biochar application to have no effect or even adverse effects on crop yield [31,32]. A meta-analysis review concluded that biochar application had a small, but statistically significant influence on crop productivity [33]. In this study, the biochar produced is used together with the recovered P-Salt, underlining the integrated concept of the project.

The combined application of P-Salt and biochar recovered from the same material has not been tested before. Based on results from the use of biochar in combination with conventional fertilizer [34–36], we assume that biochar prevents the leaching of nutrients contained in the P-Salt and increases crop yield. Biochar application may promote root development [37] through improved soil structure, resulting in more efficient nutrient uptake from the P-Salt and thus better crop development [38].

There are only a few studies [15,39,40] on the use of P fertilizer recovered from pig manure that used a comparable technique and none of these tested and compared its fertilizing effect on different crop types.

For that reason, this study aimed to test the fertilizing effect of the manure-based P-Salt on two crop types and assess its competitiveness with conventional superphosphate. A further objective was to determine whether the combined application of P-Salt and biochar improves the fertilizing effect through synergy effects. A third objective was to assess whether there are differences in the uptake efficiency of recovered and synthetic nutrients between different crop types.

Based on these objectives, the following hypotheses were set up for the study:

- P-Salts recovered as struvite from pig manure work equally well as or better than mineral P fertilizer.
- There is a synergetic effect/an interaction between P-Salt and biochar application with regard to improved soil productivity and biomass yield.
- Different crop types (cereals/legumes) react differently to P-Salt treatment, and this is also influenced by soil.

These hypotheses were tested by means of pot experiments with spring barley and faba beans. However, an important prerequisite for the use of novel products (in this case P-Salt and biochar) as fertilizers is that they do not have any undesirable effects on plants or soil biota. For this reason, a comprehensive chemical analysis and two bioassays were carried out on the products prior to the pot experiments.

2. Materials and Methods

The experimental part of this study included (1) the comprehensive determination of the chemical composition of P-Salt and biochar; (2) two bioassays to detect any eco-toxic effects on seed germination and crop development; and (3) two pot experiments to assess the fertilizing and soil-improving performance of the products.

This three-stage approach enabled detection of both desired and undesired impacts of the products on plants and soil biota at an early stage of the research project and, if necessary, the adaptation of the production process towards ecologically sound fertilizer products. Manure does not usually contain excessive amounts of problematic substances, such as heavy metals or organic pollutants. The bioassays were performed to determine whether these contaminants are concentrated in the products during the recovery process and to ensure that they do not affect crops.

2.1. Chemical Characterization

The P-Salt used in this study is a complex of struvite, magnesium phosphate and calcium phosphate obtained via the BioEcoSIM process. Pig manure was collected at a farm in Kupferzell (Germany). It was acidified with sulfuric acid to pH 5 and subsequently separated by coarse filtration into a solid and a liquid fraction. The solid fraction was dried and pyrolyzed in a superheated steam atmosphere (45 min at 450 °C). The P-Salt was recovered from the liquid manure fraction by precipitation and then filtered off. It serves as a potential source of P, but also contains N (Table 1). Contents of additional macro- and micronutrients as well as heavy metals are provided in Table A1.

Table 1. Characteristics of phosphate salts (P-Salt) and biochar.

Parameter	Unit	Method	P-Salt	Biochar
Total volatile solid content	% DM	DIN EN 15935:2012-11	17.3	-
P total	% DM	DIN EN ISO 11885	5.0	6.0
of which				
P water soluble	% DM	VDLUFA II, 4.1.4	1.2	0.4
P citric acid soluble	% DM	VDLUFA II, 4.1.3	9.5	13.5
P neutral ammonium citrate soluble	% DM	VDLUFA II, 4.1.4	9.5	13.2
N total	% DM	DIN ISO 13878	8.1	3.0
Ammonium N (NH_4-N)	% DM	DIN 38406-E5	2.4	<0.05
Nitrate N (NO_3-N)	% DM	$CaCl_2$-extraction	-	<0.00051
K	% DM	DIN EN ISO 11885	2.0	2.1
S	% DM	DIN EN ISO 11885	4.7	0.3
pH	-	DIN EN 12176	7.0	8.8

DM, dry matter; N, nitrogen; P, phosphorus; K, potassium; S, sulfur; VDLUFA, Association of German Agricultural Analytic and Research Institutes.

2.2. Toxicity Studies

Preliminary testing in petri dishes showed the germination capacity of barley to be 98% and that of faba beans to be 100%.

Two bioassays were then carried out on the P-Salt and biochar to detect any inhibiting effects on seed germination and early crop growth (Tables 2 and 3). Both tests employed a direct exposure approach. The P-Salt and biochar were applied to cress and barley at five different levels. The P-Salt applications ranged from 50% to 200% of the optimal P supply (=100%) of 150 mg P per kg substrate. The biochar application rates were calculated based on mass percentage of the cultivation substrate, not nutrient content. Both products were mixed with the substrate and filled into pots. The cress seeds were sown on top of the substrate and lightly covered. The barley seeds were sown at a depth of approximately 1 cm. The pots for the germination test were placed in a climate chamber and taken out regularly to count the number of germinated seeds. The pots for the growth test were placed on tables in a greenhouse. At the end of the test, the crops were cut 0.5 cm above the soil surface, weighed and dried at 60 °C for 48 h. Dry weight was determined and dry matter content calculated.

Table 2. Experimental set-up of seed germination test.

Crop	Cress (*Lepidium sativum*) 10 seeds per pot	Spring barley (*Hordeum vulgare* var. 'Grace') 2 seeds per pot
Substrate + pots	30 g (biochar)/50 g (P-Salt) cultivation substrate (TKS 1, Floragard) per pot (polypropylene, 7 × 7 × 8 cm^3, Goettinger)	
Treatments + replications	P-Salt: 0, 0.125, 0.25, 0.313, 0.375 and 0.5 g P-Salt per pot (control, 50%, 100%, 125%, 150% and 200% of optimal P supply); 10 replications Biochar: 0, 0.03, 0.06, 0.15, 0.3 and 0.6 g biochar per pot (control, 0.1%, 0.2%, 0.5%, 1.0% and 2.0%); 8 replications	
Duration	14 days	19 days
Conditions	20 °C, 16 h light, 8 h dark; climate chamber KBK/LS 4600 (Ehret GmbH & Co. KG, Emmendingen, Germany) Initial watering with 100 mL deionized water per pot; additional spraying when required	

TKS, the product name of the substrate.

Table 3. Experimental set-up of crop growth test.

Crop	Cress (*Lepidium sativum*) 20 seeds per pot	Spring barley (*Hordeum vulgare* var. 'Grace') 10 seeds per pot; after germination reduction to 3 seedlings per pot
Substrate + pots	250 g cultivation substrate (TKS 2, Floragard) per pot (polypropylene, 11 × 11 × 12 cm^3, Goettinger)	
Treatments + replications	P-Salt: 0, 0.375, 0.75, 0.938, 1.125 and 1.5 g per pot; 4 replications Biochar: 0, 0.25, 0.5, 1.25, 2.5 and 5 g per pot; 4 replications	
Duration	2 weeks	6 weeks
Conditions	Greenhouse; initial watering with 250 mL deionized water per pot to soak substrate; additional watering when required	

2.3. Pot Experiments

The pot experiments were carried out using two soil substrates. Clay and sand were chosen due to their low concentration and plant availability of P. The P content measured by calcium-acetate-lactate extraction (P(CAL)) in both soils is classified as very low according to Association of German Agricultural Analytic and Research Institutes (VDLUFA, Table 4). Additionally, the clay soil had a high phosphate immobilization potential due to a high concentration of carbonates. The N mineralization potential was low in both soils. Both soils were of low fertility and thus not representative of agricultural soils. The clay soil had good water retention properties, but became very hard when dry and warmed only slowly. The sand soil had zero water retention capacity; water immediately flowed to the bottom of the pots.

Table 4. Characteristics of soil substrates.

Soil	N_{min}	P(CAL)	K(CAL)	pH
	mg·(kg·soil)$^{-1}$	mg·(100·g·soil)$^{-1}$		
Clay	1.7	0.7	2.9	8.1
Sand	0.8	0.01	0.17	8.0

N_{min}, mineralized nitrogen, CAL, calcium-acetate-lactate method.

The two soils were mixed with varying amounts of P-Salt, P-Salt in combination with biochar or conventional fertilizer (Table 5). The application rates of the P-Salt were calculated based on its total P content. Optimal P supply was defined as 150 mg total P per kg·soil [41], i.e., 0.225 g P or 4.5 g P-Salt pot^{-1}, and is referred to as 100%. A reduced dose (50%) to simulate nutrient shortage and an elevated dose (200%) were included. Levels higher than 200% were not considered reasonable and thus not tested.

The performance of the P-Salt was compared to conventional mineral fertilization with ammonium nitrate NH_4NO_3 (35% N) and calcium dihydrogen phosphate $Ca(H_2PO_4)_2$, (24.6% P). Mineral N and P were applied in the same amount as in the P-Salt (Table 5). Other main plant nutrients (K, Mg, Ca) and trace elements were not considered in this experiment.

Biochar (BC) was applied in two concentrations (0.1% and 0.2%, equivalent to 1.5 and 3.0 g·pot^{-1}) in combination with the 100% level of P-Salt (Table 5). The experiment also included control pots that remained completely unfertilized. The pot experiments were carried out first with barley, then with faba beans, and with both soils for each test crop.

Table 5. Overview of all treatments and corresponding N and P application rates.

Treatment	N Applied	P Applied	Biochar
	g·pot^{-1}		
Control	-	-	-
P-Salt 50%	0.180	0.113	-
P-Salt 100%	0.360	0.225	-
P-Salt 200%	0.720	0.450	-
Mineral 100%	0.360	0.225	-
P-Salt 100% + BC 0.1%	0.360	0.225	1.5
P-Salt 100% + BC 0.2%	0.360	0.225	3.0

BC: biochar.

The required amounts of P-Salt and biochar were mixed thoroughly with 1.5 kg·soil and filled into polypropylene pots (13 × 13 × 13 cm^3, Goettinger). The conventional fertilizers (analytical grade NH_4NO_3 and $Ca(H_2PO_4)_2$) were dissolved in water to ensure exact dosage of the small amounts and then added to the soil. Pots were initially watered with 300 mL deionized water each.

The prepared pots were sown with either ten seeds of spring barley (*Hordeum vulgare* L. var. 'Grace') or eight seeds of faba bean (*Vicia faba* L. var. *minor* var. 'Isabell'). All pots were set up on a table in a greenhouse with no additional lighting in a randomized complete block design with four replications. After germination, plants were reduced to five per pot. The pots were watered from above with deionized water when necessary to keep the moisture near field capacity. Any leachates were collected and returned to the pots. Air temperature in the greenhouse was approx. 20 °C during the day and 16 °C at night.

The barley plants were treated once against powdery mildew with a combination of propiconazol, tebuconazol and fenpropidin. The bean plants were sprayed once against black bean aphids with Lambda-Cyhalothrin. Both treatments were carried out according to the manufacturer's (Syngenta Agro GmbH, Maintal, Germany) instructions for the respective crop.

After six weeks (barley BBCH 29/31, faba beans BBCH 39/51), the shoots were cut 0.5 cm above the soil surface, weighed and then dried at 60 °C for 48 h. Dry weight was determined and dry matter content calculated. Soil samples were taken from each individual pot. Roots were washed and dried at 60 °C for 48 h to determine the root dry weight.

2.4. Sample Analyses

The dried shoots were ground in a mixer mill (duration 40 s, frequency 30 min^{-1}; Retsch GmbH, Haan, Germany). Total N concentration in the biomass was determined according to DUMAS (DIN EN 13654-2). Concentrations of P, K, Ca and Mg were determined using microwave digestion followed by ICP-OES measurement (DIN EN ISO 11885). All samples were analysed in duplicate. Plant P uptake was calculated from dry matter yield (DMY) and P concentration.

The soil samples were used to determine plant-available N (NO_3 and NH_4; referred to as N_{min}) in fresh soil using $CaCl_2$ extraction followed by FIA (Flow injection analysis) measurement (DIN ISO 14255:1998-11). Plant-available P and K were then determined in air-dried soil using CAL extraction followed by flame photometer or FIA measurement, respectively (OENORM L 1087:2012-12-01). Soil pH was measured using a glass electrode after $CaCl_2$ extraction (DIN ISO 10390:2005).

2.5. Statistical Analysis

Data analysis was performed using SAS software version 9.3 PROC MIXED (SAS Institute Inc., Cary, NC, USA). Soil and treatment as well as their interaction were handled as fixed effects with DMY and nutrients in plant and soil samples as dependent variables. Data were log transformed where necessary. The graphs shown here were plotted with untransformed data. As large differences in biomass development were expected for the two soils, the treatments were compared separately for each soil. The level of significance was $\alpha = 0.05$. Standard errors (SE) given in tables were calculated as pooled standard error of the mean.

3. Results

3.1. Toxicity Studies

The growth and germination tests with biochar gave somewhat contradictory results (Tables 6 and 7). In summary, neither P-Salt nor biochar exposed any major risks to soil, crops or environment in terms of their chemical composition and resulting characteristics, as long as the amounts applied are in line with common fertilizing practice.

Table 6. Results of germination test.

	Cress	Barley
P-Salt	Seed germination up to 27% lower following application in the tested ranges.	Seed germination enhanced by up to 30% by doses up to and including the 100% dose; no further increases at higher doses.
Biochar	No effect in any of the tested concentrations.	Moderate concentrations of up to 1% did not have any negative effect.

Table 7. Results of crop growth test.

	Cress	Barley
P-Salt	Dry matter yield (DMY) was not significantly influenced by doses up to and including the 150% dose. The 200% dose resulted in 19% lower DMY compared to the control.	Tendency for decreasing DMY with increasing P-Salt dosage; however, the growth-retarding effect was only statistically significant for the two highest levels (31% and 18% lower DMY).

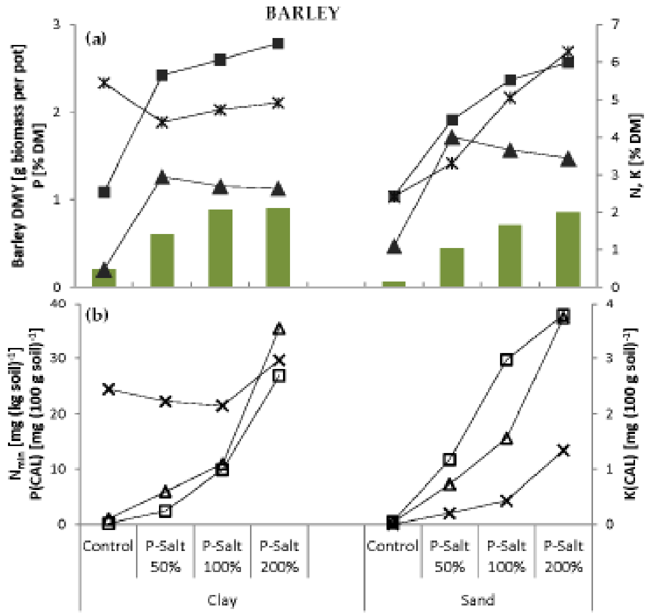
Table 7. *Cont.*

	Cress	Barley
Biochar	DMY appeared to decrease with increasing concentration. However, the adverse effect was only significant for the two highest concentrations with 19% and 20% lower DMY than in the control.	DMY not influenced by any concentration tested.

3.2. Pot Experiments

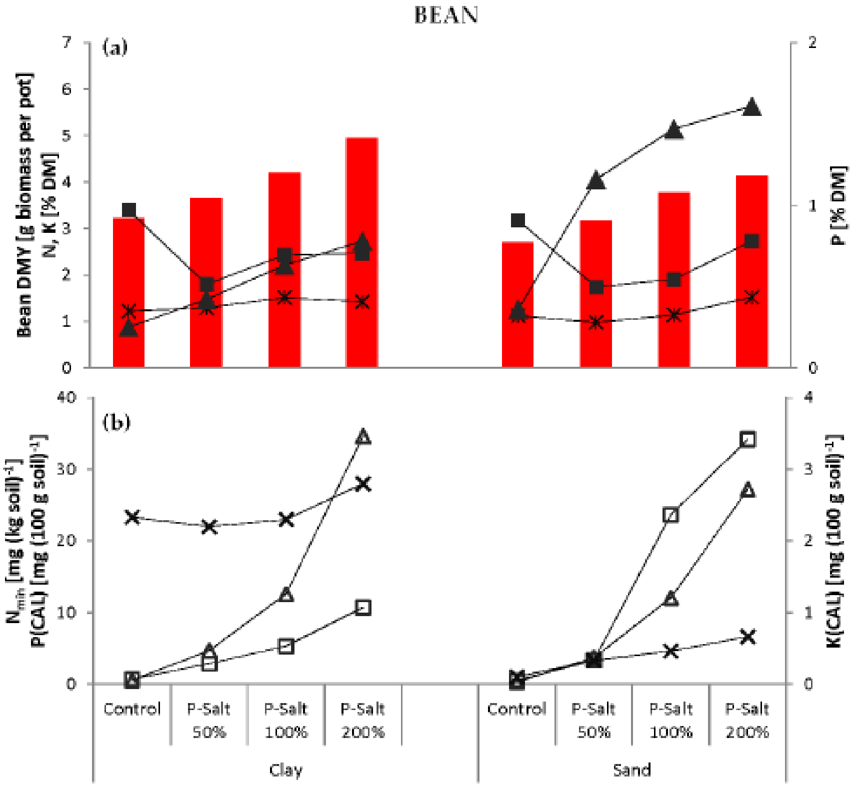
3.2.1. Effect of Increasing P-Salt Doses on Biomass Yield and Nutrient Concentrations

All P-Salt treatments led to an increase in DMY in both crops (Figures 1 and 2). In barley, this increase was significant even from the moderate 50% dose upwards, but in beans only from 100% upwards. High concentrations (200%) further increased the DMY. However, for barley this was significant only in sand, but not in clay, and for beans vice versa. The DMY of both crops was generally higher in clay than in sand. The effects of the factors 'treatment', 'soil' and their interaction 'soil*treatment' were highly significant ($p < 0.0001$) in both crops. For reasons of clarity, error bars have not been included in the figures. Instead, variances are expressed as standard errors in the corresponding tables.



		Control	P-Salt 50%	P-Salt 100%	P-Salt 200%	Control	P-Salt 50%	P-Salt 100%	P-Salt 200%	SE
		Clay				Sand				
Biomass	DMY ■	a	b	c	c	a	b	c	d	0.036
	N ■	a	b	bc	c	a	b	c	d	0.044
	P ▲	a	b	b	b	a	b	bc	c	0.038
	K ∗	a	b	bc	c	a	b	c	d	0.049
Soil	N_{min} □	a	b	c	d	a	b	c	d	0.241
	P(CAL) △	a	b	c	d	a	b	c	d	0.088
	K(CAL) ×	a	a	a	b	a	b	c	d	0.075

Figure 1. Dry matter yield (DMY) and nutrient concentration in biomass, graph upper panel, (**a**), and soil, graph lower panel, (**b**), of barley treated with increasing P-Salt levels compared to untreated control. Different letters in the table indicate statistically significant differences between treatments ($\alpha = 0.05$, $n = 4$). SE: pooled standard error of the mean.



		Control	P-Salt 50%	P-Salt 100%	P-Salt 200%	Control	P-Salt 50%	P-Salt 100%	P-Salt 200%	SE
		Clay				Sand				
Biomass	DMY ■	a	a	b	c	a	a	b	b	0.069
	N ■	a	b	c	c	a	b	b	c	0.057
	P ▲	a	b	c	d	a	b	c	d	0.026
	K ∗	a	ab	c	bc	a	a	a	b	0.041
Soil	N_{min} □	a	b	c	d	a	b	c	d	0.135
	P(CAL) △	a	b	c	d	a	b	c	d	0.076
	K(CAL) ×	a	a	a	b	a	b	c	d	0.054

Figure 2. Dry matter yield (DMY) and nutrient concentration in biomass, graph upper panel, (**a**), and soil, graph lower panel, (**b**), of faba beans treated with increasing P-Salt levels compared to untreated control. Different letters in the table indicate statistically significant differences between treatments ($\alpha = 0.05$, $n = 4$). SE: pooled standard error of the mean.

The plant N concentration showed different patterns in the two crops, although both crops showed higher values in clay than in sand. In barley, it increased with the P-Salt dosage and was highest (6.5% DM) with the 200% dose in clay. In beans, by contrast, it was relatively high in the controls (3.4% in clay, 3.2% in sand), and only between 1.7% and 2.7% DM in the treated plants. In clay, the N uptake calculated per pot puts this into perspective, where it was similar in all variants (except the 50% dose).

The plant concentration and uptake of P were higher in sand in both crops. In barley, the plant P concentration did not vary between the treatments in clay, but decreased with increasing P-Salt dose in sand. In beans, it increased steadily with P-Salt dose in both soils. The P and K concentrations were lower in beans than in barley; however, beans took up substantially higher amounts of P and K due to their higher DMY. The plant K concentration of barley grown in clay increased with P-Salt dosage. Although levels in treated plants remained below those of the control (5.4% DM), this was relativized by the higher DMY. In contrast, K increased significantly with every P-Salt level in sand. The K concentration of beans only rose with the 100% (clay) and 200% (sand) doses.

Plant-available soil nutrients measured at the end of the experiment showed the same pattern for both crops (Figures 1 and 2). The N_{min} and P(CAL) values increased significantly with P-Salt dosage in both soils, and K(CAL) only in sand. The N_{min} and P(CAL) contents were mostly higher in sand than in clay. The P(CAL) contents increased sharply from the 100% to the 200% doses. In contrast, K(CAL) contents in clay were similar for all variants except the 200% dose. Higher K(CAL) contents were found in clay than in sand.

3.2.2. Effect of Biochar Addition and Comparison of P-Salt and Mineral Fertilizer

All fertilizer treatments increased DMY in both crops compared to the control, with the one exception of the mineral fertilizer treatment of beans grown in sand (Figures 3 and 4). Biochar addition alone did not have any significant effect on DMY (Appendix A). The application of 0.1% and 0.2% biochar in addition to P-Salt enhanced barley DMY compared to fertilization with P-Salt only; however, this effect was only statistically significant in sand (Figure 3). All P-Salt treatments—with or without biochar—outperformed the mineral fertilizer in terms of DMY, except for beans grown in clay. In sand, it was not possible to harvest any barley biomass from pots treated with mineral fertilizer. The highest DMY overall was obtained with the P-Salt + 0.1% BC treatment (4.5 g·pot^{-1} for bean grown in clay; 1.0 g·pot^{-1} for barley grown in sand).

The highest plant N concentration was found in the minerally fertilized plants (7.0% DM in barley, 6.9% DM in beans), followed by the P-Salt treatment in barley and the biochar variants in beans. However, the N uptake in barley was lower with mineral fertilizer than with the P-Salt treatments (Table 8). The N concentration seemed remarkably high in minerally fertilized beans grown in sand, but this was partly an effect of the lower DMY.

The plant P concentration was higher in sand than in clay. There was no difference between the P-Salt alone and the combined treatments with biochar in barley in either soil (on average 1.2% DM in clay, 1.5% DM in sand). Mineral fertilizer considerably increased plant P (to 2.8% DM) in barley grown in clay, whereas it decreased plant P in beans in both soils.

In both crops and soils, the highest plant K concentration was found in plants treated with the combination of P-Salt and 0.2% biochar. Biochar addition almost always significantly increased plant K relative to P-Salt alone and mineral fertilizer. Application of P-Salt with and without biochar resulted in a higher uptake of K than with mineral fertilizer.

By far the highest N_{min} contents were found in minerally fertilized pots in both crops and soils. These were followed by the P-Salt variants, but with much lower values. Again, higher values were found in sand. Biochar addition, particularly the 0.2% concentration, seemed to lower N_{min} compared to P-Salt alone.

Soil P(CAL) was close to zero in all controls and continuously increased following P-Salt and particularly biochar treatments. The P(CAL) of pots treated with mineral fertilizer was between the control and P-Salt variants, yet unexpectedly low.

The K(CAL) values closely followed the pattern of plant K: highest values were found in pots treated with P-Salt and 0.2% biochar and lowest values in minerally fertilized pots. Application of P-Salt alone and each of the combinations significantly increased K(CAL). Levels were generally higher in clay than in sand. Practically no K(CAL) was measured in sand in the control (0.0 mg·(100·g·soil)$^{-1}$) and the minerally fertilized pots (0.1 and 0.2 mg·(100·g·soil)$^{-1}$ for beans and barley, respectively).

3.2.3. Influence of Fertilizer Form on Nutrient Uptake

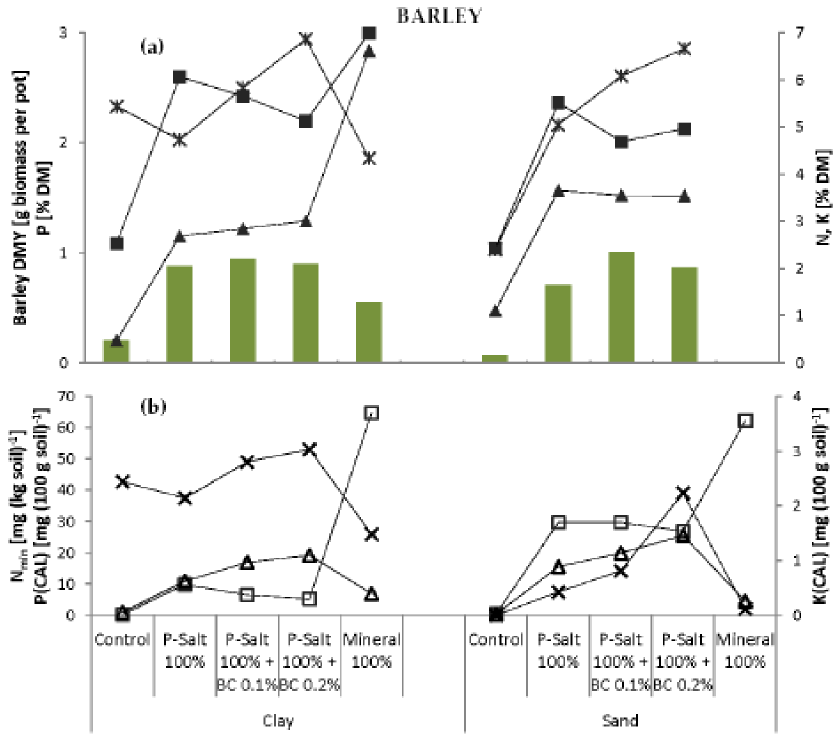
The N uptake of barley was higher from the P-Salt treatments than from mineral fertilizer. For P uptake, it was the other way around. This was observed in both soils (Table 8).

The nutrient uptake of beans was the reverse for both N and P. The nutrient uptake was of course closely related to the DMY obtained and the concentration of N and P in the crops (Figures 3 and 4).

3.2.4. Influence of Treatment and Soil on Root Dry Matter and Shoot:Root Ratio

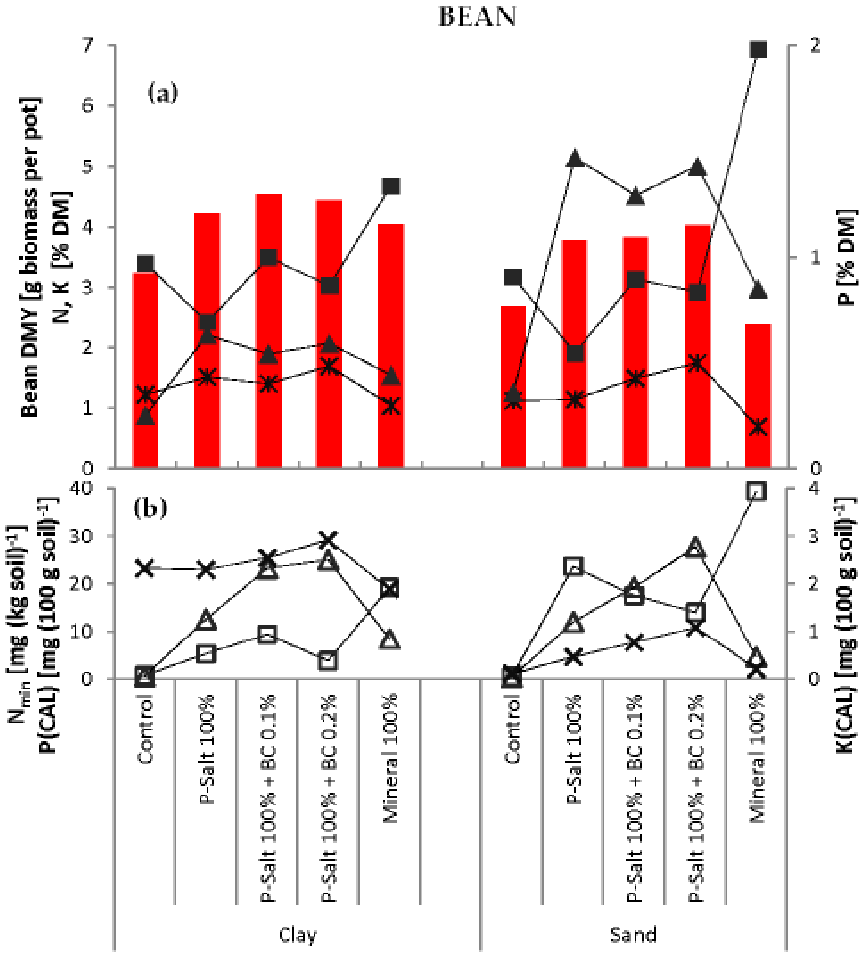
As expected, the root development of barley was much more pronounced in sand soil than in clay (Table 9). In sand, even the smallest plants had developed a relatively extensive root system. This is reflected by the low shoot:root ratio. In clay, the two biochar treatments led to a particularly high shoot:root ratio (>9).

In contrast, beans formed more root biomass in clay than in sand and in general considerably more than barley. The shoot:root ratio of the beans followed the same pattern for all treatments in both soils; however, values reached a slightly higher level in sand.



		Control	P-Salt 100%	P-Salt 100% + BC 0.1%	P-Salt 100% + BC 0.2%	Mineral 100%	Control	P-Salt 100%	P-Salt 100% + BC 0.1%	P-Salt 100% + BC 0.2%	Mineral 100%	SE
				Clay					Sand			
Biomass	DMY ■	a	b	b	b	c	a	b	c	c	-	0.036
	N ■	a	b	b	c	d	a	b	c	c	-	0.044
	P ▲	a	b	b	b	c	a	b	b	b	-	0.038
	K ∗	a	b	a	c	b	a	b	c	c	-	0.049
Soil	N_{min} □	a	b	c	c	d	a	b	b	b	c	0.241
	P(CAL) △	a	b	c	c	d	a	b	c	d	e	0.088
	K(CAL) ×	ab	a	bc	c	d	a	b	c	d	e	0.075

Figure 3. Dry matter yield (DMY) and nutrient concentration in biomass, graph upper panel, (**a**), and soil, graph lower panel, (**b**), of barley treated with P-Salt only ("P-Salt 100%"), P-Salt and biochar ("P-Salt + BC 0.1%", "P-Salt + BC 0.2%") and mineral fertilizer ("Mineral 100%") compared to untreated control. Different letters in the table indicate statistically significant differences between treatments (α = 0.05, n = 4). SE: pooled standard error of the mean.



		Control	P-Salt 100%	P-Salt 100% + BC 0.1%	P-Salt 100% + BC 0.2%	Mineral 100%	Control	P-Salt 100%	P-Salt 100% + BC 0.1%	P-Salt 100% + BC 0.2%	Mineral 100%	SE
		Clay					Sand					
Biomass	DMY ■ (red)	a	b	b	b	b	a	b	b	b	a	0.069
	N ■	ab	c	a	b	d	a	b	a	a	c	0.057
	P ▲	a	b	c	bc	d	a	b	c	b	d	0.026
	K ✳	a	bc	ac	b	d	a	a	b	c	d	0.041
Soil	N_{min} □	a	b	c	d	e	a	b	c	c	d	0.136
	P(CAL) △	a	b	c	c	d	a	b	c	d	e	0.076
	K(CAL) ×	a	a	a	b	c	a	b	c	d	e	0.054

Figure 4. Dry matter yield (DMY) and nutrient concentration in biomass, graph upper panel, (**a**), and soil, graph lower panel, (**b**), of faba beans treated with P-Salt only ("P-Salt 100%"), P-Salt and biochar ("P-Salt + BC 0.1%", "P-Salt + BC 0.2%") and mineral fertilizer ("Mineral 100%") compared to untreated control. Different letters in the table indicate statistically significant differences between treatments (α = 0.05, n = 4). SE: pooled standard error of the mean.

Table 8. Mean nutrient uptake into shoots for fertilizer forms with/without biochar (BC) addition tested. Different letters in the table indicate statistically significant differences between treatments ($\alpha = 0.05$, $n = 4$).

			Clay					Sand					SE
			Control	**P-Salt 100%**	**P-Salt 100% + BC 0.1%**	**P-Salt 100% + BC 0.2%**	**Mineral 100%**	**Control**	**P-Salt 100%**	**P-Salt 100% + BC 0.1%**	**P-Salt 100% + BC 0.2%**	**Mineral 100%**	
Barley	N	$mg \cdot pot^{-1}$	5.13a	53.48b	53.37b	41.69bc	38.11c	1.64a	38.88b	46.88b	43.20b	no crop	0.138
	P		0.41a	10.17b	11.48b	11.59b	15.46c	0.32a	11.04b	13.74c	11.69b	no crop	0.145
	K		11.02a	41.71b	54.96bc	61.78c	23.64d	1.63a	35.60b	60.83c	57.96c	no crop	0.166
Bean	N	$mg \cdot pot^{-1}$	109.69a	102.24a	158.47b	117.83a	189.14c	85.56a	71.89b	119.48c	117.86c	165.11d	0.077
	P		8.08a	26.52b	24.48b	26.21b	17.80c	9.70a	55.57b	49.18b	57.63b	20.25c	0.085
	K		39.41a	63.57b	63.46bc	69.71c	42.07a	30.18a	43.09b	56.81c	70.12d	16.44e	0.091

SE: pooled standard error of the mean.

Table 9. Mean root dry matter and shoot:root ratio of barley and faba beans for fertilizer forms with/without biochar (BC) addition tested. Different letters in the table indicate statistically significant differences between treatments ($\alpha = 0.05$, $n = 4$).

		Unit	Clay					Sand					**SE**
			Control	**P-Salt 100%**	**P-Salt 100% + BC 0.1%**	**P-Salt 100% + BC 0.2%**	**Mineral 100%**	**Control**	**P-Salt 100%**	**P-Salt 100% + BC 0.1%**	**P-Salt 100% + BC 0.2%**	**Mineral 100%**	
Barley	Root dry matter	$g \cdot pot^{-1}$	0.22ns	0.19ns	0.10ns	0.11ns	0.14ns	0.42a	0.44a	0.66b	0.40a	no crop	0.067
	Shoot:root ratio	-	1.01a	4.42b	9.83c	9.64c	4.20b	0.16a	1.79b	1.65b	2.88b	no crop	0.180
Bean	Root dry matter	$g \cdot pot^{-1}$	4.65b	4.37b	4.20b	5.05b	3.11a	2.00a	2.66b	2.78b	3.02b	1.60a	0.087
	Shoot:root ratio	-	0.71a	1.00bc	1.13cd	0.96ab	1.37d	1.35ab	1.45ab	1.49ab	1.33a	1.50b	0.114

SE: pooled standard error of the mean, ns: not significant.

4. Discussion

The findings of this study confirmed the hypotheses that (1) the fertilizing performance of P-Salt recovered from manure is equivalent to that of mineral P fertilizer; (2) there are positive synergies between biochar and P-Salt; and (3) there are differences in reaction to fertilization between crops. These are discussed in the following sections.

4.1. The Fertilizing Performance of P-Salt Is Equivalent to that of Mineral P Fertilizer

The fertilizing performance of P-Salt was evaluated on the basis of DMY and nutrient concentration. In terms of DMY, P-Salt performed better than mineral P fertilizer in both barley and bean crops and in the two soils sand and clay. This is particularly remarkable, as the fertilizers were compared based on total rather than water-soluble P content. The latter differed considerably, with commercial triple superphosphate supplying 43.5% and P-Salt only 1.2% of P in water-soluble form. Analysis by Mazeika et al. [42] of the molecular and morphological structure of manure-derived fertilizer (poultry manure) showed a colocalization of K, S, and P within the derived organo-mineral fertilizers (OMF). This, and the specific structure of the OMF at the molecular and crystalline levels may affect their performance, which can thus be different than that of minerally-derived P fertilizer.

Although barley had a higher DMY with P-Salt fertilization, its P uptake was higher with mineral fertilizer. We concluded that this is an effect of the large water-soluble P-fraction in mineral fertilizer. We hypothesize that in general both fertilizer types have similar yield effects, but that they are based on different dynamics of P-availability over time.

Contrary to expectations, both P concentration and uptake were higher in beans from the P-Salt treatment than from the conventional fertilizer treatment. As a legume, the bean was able to stimulate P mobilization by releasing root exudates, which very likely increased P availability [16] from the P-Salt.

Previous studies comparing P fertilizers/struvites recovered from various materials to commercial P fertilizer have reported that the recycled products increased DMY in maize [20], led to comparable DMY in perennial ryegrass [22], or at least improved DMY compared to untreated controls in several crops [17–19,43].

Our findings support the hypothesis that P-Salt is able to compete with commercial products in terms of yield effect and nutrient supply under the conditions tested.

However, we observed a few potential disadvantages of P-Salts compared to mineral fertilizer. The increase in both P and N concentration in barley biomass was considerably higher with mineral fertilizer. This can most likely be attributed to the higher plant-availability of P and N from mineral fertilizer immediately from the beginning of the experiment. These plants probably took up all their required nutrients within the first weeks. In contrast, the crops receiving P-Salt—whose main component struvite is known for its gradual P release [16] and low solubility—were not able to catch up within the remaining time. However, they compensated for the lower nutrient concentration through higher DMY, resulting in a type of nutrient dilution effect. A test duration longer than six weeks may have produced slightly different results, particularly because the amount of plant-available P from both fertilizer types may then have equalized.

In general, the fertilizing effect of mineral fertilizer was more uniform than that of P-Salt. This was apparent from the lower standard deviation of the DMY between replications. The reason for this remains unclear. To ensure a sufficiently uniform distribution, the P-Salt was ground very finely before mixing it with the soil. Fine particle size can positively influence the nutrient availability and thus the fertilizing effect [44]. For future experiments, granulation of the P-Salt should be considered to prevent possible demixing.

4.2. Biochar Improves P-Salt Fertilization Effects

The results of this study confirmed the findings of Schulz and Glaser [36] that biochar enhanced the effects of fertilizer and led to an increase in yield. In addition, we found that the biochar effect differed depending on soil and its positive effect appeared to increase with decreasing soil organic matter and an increasing sand content. Therefore, it was concluded that biochar has huge potential as a soil improver, particularly for more unproductive soils with low organic matter content, such as sand.

Light soils are more often subject to nutrient leaching due to lack of organic matter. Biochar addition may prevent these losses by improving the physical properties of the soil, namely the nutrient and water retention capacity of the soil [45], both valuable in sand. Biochar can absorb considerable amounts of water due to its large specific surface area. This water then remains available for the crops, along with the nutrients dissolved in it. However, the subsequent increased root growth reported by Bruun et al. [45] was only seen to a small extent in this study. The shoot:root ratio of the biochar variants significantly increased in barley grown in clay. This could be an indication of P accumulation in the soil. An increase in soil pH following biochar application [46] can have the indirect effect of higher P availability. This, in combination with the direct effect of a small amount of P from the biochar itself, results in improved P uptake and increased growth [47]. There are certainly interactions between the physical and the biological effects, but it was not possible to draw a conclusion here.

Towards the end of the study, significantly increased contents of P(CAL) and K(CAL) were recorded following biochar application in both crops and soils, which for P is consistent with previous studies [48,49]. The same was observed for plant K concentration and uptake. Hence, the biochar served as a source of P and K for the crops, despite the fact that the analysis found the P contained in the biochar to have very low water solubility. Biochars made from solid manures [1], poultry litter and swine manure [50] or beech-wood [36] are often reported to act as a nutrient source.

Biochar's normally positive property of retaining nutrients, thus preventing them from leaching can of course also have the negative effect of immobilization and therefore reduced plant-availability of certain nutrients. The treatments with biochar had lower soil N_{min}. Although these pots received the same amount of N as those in the "P-Salt only" treatments, it was not entirely plant-available. This suggests the—at least temporary—immobilization of nitrogen by biochar, as also observed in other studies (e.g., [34,35,37,48]). Beans showed a higher plant N concentration in the combined treatments than with P-Salt alone, whereas barley was unable to maintain the N concentration level of the P-Salt treatment. Although the bean seeds were not inoculated with rhizobia, by harvest, N fixation nodules had developed in the majority of pots. Thus, beans were able to meet their N demand by taking up additional N from biological fixation and possibly also mobilizing the N bound to biochar.

It is possible that biochar applied in combination with fertilizer binds nutrients released by the fertilizer. The nutrient release from P-Salt is slow. Therefore, it is assumed that biochar binds fewer nutrients from P-Salt than from mineral fertilizer, which provides the entire nutrient amount applied in readily plant-available forms. Enhanced DMY following the combined application of biochar and P-Salt may be explained by reduced nutrient leaching [48]. Furthermore, this result must stem from a synergistic effect, as the combined application led to higher DMY than with application of either P-Salt or biochar alone (Table A2, [36]). Therefore, it can be concluded that the fertilizing effect of P-salt can be enhanced by combined application with the biochar—a by-product of the BioEcoSIM process. The two biochar concentrations applied in this study did not significantly differ in terms of DMY. However, the 0.2% concentration showed a trend to decreasing DMY in barley in both soils and beans grown in clay. As biochar concentrations ten times as high (1% and 2%) did not show any adverse effect in the preliminary bioassays, a toxic effect of the low concentrations in the main experiment can be discounted. Bruun et al. [45] concluded that rates of 1%–2% by mass improve soil quality. The slight, but statistically insignificant decreases in yield following the 0.2% concentration may be in some way related to limited plant-availability of nutrients as discussed above.

In summary, the positive yield effect of biochar in sand was probably a consequence of factors such as improved soil structure (including water retention and increased soil organic matter), retention of fertilizer nutrients and limited nutrient supply. In combination, this promoted crop growth and yield.

4.3. Crop Types (Cereals/Legumes) React Differently to the P-Salt Treatment

The essential difference between the crop types was the significantly higher positive effect of P-Salt on cereal than legumes. This is revealed by a comparison of the controls with the P-Salt variants. Barley showed a highly positive reaction to N and P supplied by the P-Salt in terms of DMY and both plant concentration and uptake of N and P. Beans, in contrast, produced the same DMY in the control and the 50% treatment. The extremely low soil N_{min} and P(CAL) in the controls recorded at the beginning of the experiment suggests that beans were able to meet their nutrient demands using other sources, for example atmospheric N.

The main explanation here is of course that the bean as a legume has the ability to (1) take up additional N from biological fixation; and (2) mobilize P with low plant availability by releasing organic acids. The latter, for instance, has been reported for the uptake of native soil P by white lupin *Lupinus albus* L. [51].

In addition, the bean has a higher thousand grain weight than barley, providing more nutrients and thus making it less dependent on external nutrient supply during germination and early growth stages. Cereals, in contrast, develop an extensive root system to ensure access to nutrients provided both by the soil and by fertilizer [52].

The moderate DMY response to the P-Salt treatments as well as the lower plant N concentration in beans might be explained by inhibited biological N fixation as a consequence of applied N. This can also cause yield losses [53], yet this was not observed. The benefit of N fertilization of legumes is controversial, although minor N fertilization is sometimes recommended for faba bean production under unfavourable growing conditions, poor seedbed environment or low soil pH.

In sum, the different reactions are ascribable more to the crop type than to the P-Salt. For beans, it would be recommendable to modify the precipitation process in order to obtain a P-Salt with lower N content. We conclude that P-Salt worked well for both crop types tested, supporting the hypothesis that P-Salt could replace conventional P fertilizer.

5. Conclusions and Recommendations

This study explored the potential use of a P-Salt recovered from pig manure as a replacement for conventional mineral P fertilizer.

The P-Salt was found to have the same or even better effects than mineral fertilizer on growth in both crops in both soils. Thus, firstly, the recovered product can replace conventional mineral P in terms of the fertilizing effect for the two crop types tested here. Secondly, and perhaps more importantly, the demand for P fertilizer in European agriculture could theoretically be met by P recycling from manure alone. Ideally, this would render the extraction of "new" P from rock phosphate for fertilizer production superfluous in the medium to long term.

This study did not consider the potential fertilizer replacement value of the P-Salt. Organic products are usually applied in higher amounts in order to compensate for the slower release and lower plant availability of nutrients than with conventional products. If the amounts applied had been adjusted accordingly, the P-Salt would have certainly led to considerably better results than those obtained in this study. In addition, the P-Salt can supply plants and soil with additional microelements and a small amount of organic matter. These aspects render P-Salt recovered from manure by the BioEcoSIM process even more advantageous than conventional fertilizers.

However, the acceptance of such recycled fertilizers by agriculture and horticulture is currently fairly low. One constraint is certainly the reliability of the novel product. The combination of P-Salt and conventional products could serve as a convincing solution for users/farmers: conventional fertilizer provides readily available, water-soluble P in the early growth stages, whereas the slow-releasing P-Salt ensures a continuous supply during the entire growth period. This would allow the entire P fertilizer amount to be administered in one application without the risk of P deficiency in heavy soils with high P immobilization potential (e.g., clay) of water-soluble P. P-Salt also has a strong advantage in light soils with low buffer capacity (e.g., sand) where the slow release of P prevents its leaching or surface runoff. The fertilizing effect of P-Salt can be enhanced by combined application with biochar, which is also a product of the manure recycling process in which P-Salts are extracted.

The results indicate that biochar improves the soil status of sand, suggesting that biochar can be a valuable addition to sandy or degraded soils. However, no significant benefit was seen in the clay soil.

Granulation or pelletizing of finely ground P-Salt and biochar can considerably simplify their handling and turn them into marketable products. A reduction in N content of the P-Salt would avoid the accompanying N application, thus increasing flexibility. The next steps will be a detailed assessment of how the properties of the raw manure influence the emerging products and validation of the presented findings in field-scale experiments.

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Appendix A

Table A1. List of additionally analysed parameters measured in phosphate salts (P-Salt) and biochar and methods used.

Parameter	Unit	Method	P-Salt	Biochar
Calcium (Ca)	% DM	DIN EN ISO 11885	3.3	8.3
Magnesium (Mg)	% DM		2.7	3.9
Sodium (Na)	mg/kg		17,600	5,310
Boron (B)	mg/kg		39.1	98.2
Cobalt (Co)	mg/kg		<5.00	5.52
Manganese (Mn)	mg/kg		588	1070
Molybdenum (Mo)	mg/kg		15.3	10.9
Selenium (Se)	mg/kg	DIN EN ISO 17294-2 (E29)	5.8	<2.0
Iron (Fe)	mg/kg	DIN EN ISO 11885	2200	2300
Aluminium (Al)	mg/kg		280	870
Lead (Pb)	mg/kg		<5.0	<5.0
Cadmium (Cd)	mg/kg		0.6	<0.5
Chrome (Cr)	mg/kg		5.9	11.0
Copper (Cu)	mg/kg		226	158
Nickel (Ni)	mg/kg		8.2	7.9
Zinc (Zn)	mg/kg		2390	1500
Arsenic (As)	mg/kg		<4.0	<4.0
Thallium (Tl)	mg/kg	DIN EN ISO 17294-2 (E29)	0.3	<0.2
Mercury (Hg)	mg/kg	DIN EN 1483-E12-4	0.07	<0.05

DM, dry matter; DIN, German Organization for Standardization; EN, European Standard; ISO, International Standards Organization.

Table A2. Mean dry matter yield (DMY) of barley and bean treated with increasing biochar (BC) concentrations (n = 4).

		Clay				Sand			
		Control	0.1% BC	0.2% BC	0.5% BC	Control	0.1% BC	0.2% BC	0.5% BC
Barley	g·pot^{-1}	0.20	0.28	0.29	0.24	0.07	0.11	0.15	0.13
Bean	g·pot^{-1}	3.23	3.23	3.87	3.80	2.70	2.83	2.95	3.53

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3 Phosphates recycled from semi-liquid manure and digestate are suitable alternative fertilizers for ornamentals

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Phosphates recycled from semi-liquid manure and digestate are suitable alternative fertilizers for ornamentals

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ABSTRACT

In several regions in Europe, the amounts of both manure produced by pig husbandry and biogas digestates from anaerobic digestion are too high to be sustainably applied to the surrounding fields. In these regions, nutrient surpluses are therefore often a problem. The research projects GOBi and BioEcoSIM succeeded in developing innovative recycling technologies for the recovery of phosphorus (P) from biogas digestates and manure, converting them into valuable fertilizers. This study tested the suitability of recovered phosphate salts ("P-Salts") and dried solids as P fertilizers for sunflower, marigold and Chinese cabbage in a greenhouse experiment. Treatments included two recovered P-Salts (from manure and digestate), two dried solids (air-dried and steam-dried), a combination of salt and solid, and triple superphosphate (TSP) as reference, each at two fertilization levels. Measurements included biomass production (ornamentals separated into shoots and flowers), P concentration in the biomass and plant-available P in the growing medium. Both P-Salts had more or less the same effect as TSP on biomass production. The combination of P-Salt and air-dried solids resulted in a synergistic effect on sunflower in terms of biomass yield, P concentration and number of flowers. The P concentration was mostly higher in plants treated at the higher P fertilizer level.

A fast P uptake into plants and thus high plant availability is particularly important in the horticultural sector due to the short production periods of potted plants. In general, all the tested recycled products except the air-dried solids could be adapted to the requirements of different ornamentals, met their P demand as efficiently as TSP and thus have high potential as P fertilizers. The P-Salts are more suitable for short-term and the steam-dried solids more for long-term P supply. The combination of both may ensure optimal P supply and guarantee long-term product quality.

1. Introduction

Phosphorus (P) is required for good flowering quality and quantity of ornamental plants. Nowadays, it is mainly applied in the form of fertilizer manufactured from phosphate-rich rocks. It is well-known that fossil P resources are limited. Assuming future consumption continues to increase at a constant rate, the economically exploitable reserves will be exhausted in about 350 years (USGS, 2016). Total resources are estimated to last up to 1300 years (USGS, 2016). However, there is a high degree of uncertainty in this prediction as it includes all naturally occurring material for which an economic extraction is currently or potentially feasible. Today, the entire P requirements for chemical fertilizers and feed are derived from phosphate-rich rocks. About 75% of the identified global reserves are located in Morocco (Western Sahara), which is also the main exporter of phosphate ore (Schoumans et al., 2015). Koppelaar and Weikard (2013) reported that 17.6 Mt of P were utilized in fertilizer production in 2009, representing more than 80% of the total mined P. The manufacturing process of chemical P fertilizers produces waste that contaminates soil and water resources and the use of these fertilizers contributes to heavy metal contamination of soils, resulting in increased expenses for soil remediation (Moura Filhio and Dantas Alencar, 2008).

The high demand for phosphate fertilizers in food and flower production makes finding affordable alternative products crucial. Such alternatives should be available in relatively high quantities, have consistent quality and equivalent fertilization effects and plant nutrient availability to conventional fertilizers.

One possibility is the recycling of P from manure and biogas digestates produced in agriculture. The accumulation of large amounts of

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semi-liquid manure is a particular problem in regions with intensive livestock production. Moreover, livestock husbandry is often found in combination with anaerobic digestion as an efficient method of converting animal manures into biogas and heat by co-fermentation with energy crops (Nkoa, 2014), resulting in biogas digestates. In Germany, the amount of biogas digestates is estimated to be around 65.5 million m^3 per year (Möller and Müller, 2012). The quantities of manure and digestate produced are likely to increase in future due to ongoing intensification in livestock breeding, worldwide trends in energy consumption and the predicted need for a 30% increase in energy production in the next 25 years, especially from renewable energy (IEA, 2015).

Both manure and digestates are particularly nutrient-rich and their positive effect on crop growth has frequently been demonstrated. These positive effects are mainly attributed to the supply of nitrogen and phosphate (Alburquerque et al., 2012), and the return of organic matter (Möller and Müller, 2012).

However, farmers are often reluctant to use organic fertilizers as the release of nutrients is slower and more weather-dependent compared to soluble chemical fertilizers (Figueiredo et al., 2008). In addition, the high water content (around 90%) of manure and digestates (Risberg et al., 2017) makes the application of large quantities per hectare necessary and renders the handling and transport in horticulture challenging. Moreover, untreated anaerobic digestate may not always be a perfect organic fertilizer due to its unbalanced nutrient ratio (Westerman and Bicudo, 2005) and specific requirements for soil application techniques as a consequence of the increasing necessity to avoid ammonia losses (Kreith and Tchobanoglous, 2002; BMEL, 2017).

In order to produce fertilizers with reduced volume that can be easily stored, transported and applied, efficient solutions are required to increase the nutrient content and decrease the water content of residues such as digestates and manure. The plant availability of P in recovered products is often low, or at least unpredictable (Kahiluoto et al., 2015). Bilbao et al. (2017) have developed a recovering process for manure and digestates in which 95% of the insoluble P is first converted into a dissolved form. The pretreated manure or digestate is then subjected to a solid-liquid separation. Phosphate salts (P-Salts) are obtained from the liquid fraction by precipitation. The resulting P-Salts are in the form of a powder that can be dried and granulated and, as such, are easy to dose and mix with horticultural growing media. The separated solid fractions of digestate and manure are also dried and used as organic P fertilizer with a texture comparable to wood shavings.

All of these recycled P-fertilizers are expected to have a high potential as alternative P-fertilizers (Bilbao et al., 2017); the manure-based P-Salt has already been found suitable for barley and faba bean (Ehmann et al., 2017). As horticulture is a business which is fairly location-independent, particularly the protected production in greenhouses, a dry and transportable form of recovered P fertilizers would be of considerable interest. The P-Salts and dried solids can be applied separately or in combination. The combined application of mineral and organic fertilizers in the form of TSP and compost was shown to result in increased plant P availability in a greenhouse study with maize (Muhammad et al., 2007). For this reason, we included a combination of P-Salt and dried solids in order to evaluate a potential synergy effect of these two components. This combined treatment may also provide a nutrient ratio more suited to the crops' requirements.

The recycled P fertilizers were tested in a greenhouse experiment with, sunflower (*Helianthus annuus* L.) and marigold (*Tagetes erecta* L.), both of which are among the most prominent ornamentals in Germany. Sunflower ranks fifth in sales of cut flowers in Germany, with a volume of 120 Mio. € per year (AMI, 2016). Marigold, a member of the family *Asteracaea* or *Compositae*, is an important commercial flower that is gaining popularity on account of its easy cultivation and wide adaptability (Asif, 2008). Both plants are marketed as cut flowers and potted flowers. Marigolds are often used for flower beds and for making garlands. Single sunflowers grown and sold in pots achieve high profit margins.

Chinese cabbage (*Brassica campestris* L. var. pekinensis Lour (Olson)) was included as a P sensitive indicator test crop. Symptoms of P deficiency are shown immediately through purpling of the leaves. Crops of the *Brassica* genus are among the ten most important vegetables in economic terms on global agricultural markets. Chinese cabbage is a cole crop plant and is an important fresh and processed vegetable, especially in Asian countries. In 2016, approx. 38.000 t were produced on 850 ha in Germany (Destatis, 2017).

The objectives of this study were: 1) to test the suitability as P fertilizers of P-Salts recovered from semi-liquid pig manure and biogas digestates and of dried solid fractions of non-treated digestates in two ornamentals and one vegetable; 2) to assess the competitiveness of these alternative P fertilizers compared to conventional superphosphate; 3) to determine whether the combined application of P-Salt and dried solid digestate improves the fertilizing performance through synergy effects; and 4) to assess the role of P fertilization in the flowering of sunflower and marigold, comparing the effect of the recycled fertilizers and commercial TSP.

Based on these objectives, the following hypotheses were set up:

- The effect of P-Salts recovered from semi-liquid manure and digestates, and the two dried solid fractions on biomass production and P concentration of sunflower, marigold and Chinese cabbage is equivalent to that of the conventional P fertilizer triple superphosphate (TSP).
- The combination of P-Salt and separated solids has a synergistic effect on plant growth.
- Recycled fertilizers enhance flowering in the same way as TSP and the level of P influences the number of flowers

These hypotheses were tested by means of a pot experiment with sunflower, marigold and Chinese cabbage.

2. Material and methods

2.1. Production of P-Salts and solids from pig manure and biogas digestate

The P-Salts were recovered from acidified semi-liquid pig manure (P-Salt_manure) and biogas digestate (P-Salt_digestate) as described by Bilbao et al. (2017). The dried solids were obtained from untreated digestate purely through solid-liquid separation. The solid fraction was dried either in warm air at 40 °C (air-dried solids) or with superheated steam at 120 °C (steam-dried solids).

The P-Salts had P concentrations approximately 5 times higher than the dried solids (Table 1). Soluble plant-available P fractions were determined for all products, Hedley fractionation was only performed for the digestate-based products (Tables 2 and 3). Both P-Salts are mixtures of magnesium ammonium phosphate (struvite) and calcium phosphates. The P-Salt_manure also contained 2.4% N, 1.3% K, 10.0% Ca and 4.8% Mg and the P-Salt_digestate 1.3% N, 1.0% K, 17.0% Ca and 5.0% Mg in the fresh matter.

Table 1
P concentration of the fertilizers.

Fertilizer	Acronym	Dry matter in % FM	P in % FM
P-Salt recovered from semi-liquid pig manure	P-Salt_manure	68.6	10.5
P-Salt recovered from digestate	P-Salt_digestate	69.7	10.7
Steam-dried separated solids from digestate	Steam-dried solids	91.6	2.3
Air-dried separated solids from digestate	Air-dried solids	95.4	2.1
Mineral P fertilizer as reference (Triple superphosphate)	TSP	–	19.0

FM, fresh matter; dry matter determined according to DIN EN 12880; P determined according to DIN EN ISO 11885.

Table 2
Total and soluble P, total organic carbon and pH of the fertilizers.

Property	P-Salt_manure	P-Salt_digestate	Steam-dried solids	Air-dried solids	Method
P_{total} in % FM	10.5	10.7	2.3	2.1	DIN EN 12880
Water-soluble P in % FM	0.28	0.13	0.35	0.35	VDLUFA II, 4.1.4
Neutral ammonium citrate-soluble P in % FM	11.47	10.42	0.90	1.06	VDLUFA II, 4.1.4
Formic acid-soluble P in % FM	11.38	10.12	0.92	1.06	VDLUFA II, 4.1.2
Citric acid-soluble P in % FM	11.42	10.38	0.92	1.07	VDLUFA II, 4.1.3
Mineral acid-soluble P in % FM	11.47	10.46	1.00	1.11	VDLUFA II, 4.1.1.4
Total organic carbon in % FM	1.43	3.58	38.90	38.40	VDLUFA II, 10.2
pH in $CaCl_2$	7.9	8.3	8.5	7.1	DIN EN 12176

Table 3
Total and fractionated P of the digestate-based products.

Variable	P-Salt_digestate	Steam-dried solids	Air-dried solids
P_{total} in % FM	10.7	2.3	2.1
Sequentially fractionated with … in mg P (g DM)$^{-1}$ *			
… $NaHCO_3$ (easily available P)	29.9	6.7	7.5
… NaOH	6.3	1.0	1.3
… H_2SO_4 (sparingly available P)	53.3	1.0	1.7

* Determined using a modified Hedley fractionation method (Hedley et al., 1982; Tiessen and Moir, 1993; Redel et al., 2013).

Table 5
Supply target of main nutrients N, P and K in the growing medium.

Nutrient	Sunflower	Marigold	Chinese cabbage
	mg L^{-1} growing medium		
Full supply of P (optimal)*	261.6	130.8	87.2
Reduced supply of P (low)*	130.8	65.4	43.6
Mineral N**	800.0	400.0	800.0
K	830.2	415.1	830.2

* P in growing medium not considered.
** CAT-extractable mineral N and K in growing medium considered (only difference applied).

2.2. Description of the pot experiment

A greenhouse pot experiment assessed the P fertilizing effect of 1) P-Salts recovered from biogas digestate and semi-liquid manure; 2) two different types of dried solids from the separated solid fraction of digestate; and 3) a combination of P-Salt_digestate and air-dried solids; each compared to a conventional mineral fertilizer.

The growing medium used was chosen specifically because it had the lowest P concentration of all media available (Table 4).

The growing medium was thoroughly mixed with varying amounts of P-Salts, solids, a combination of P-Salt and solids, or triple superphosphate (TSP) and filled into pots. The application rates of the P fertilizers were adapted to the optimal P supply for each of the three test species: sunflower, marigold and Chinese cabbage (Table 5). Phosphorus in the growing medium was not considered as it was very low. In the combined treatments, 50% of the P was applied as P-Salt_digestate and 50% as air-dried solids. In addition, a reduced P dose (50%) was included for all treatments to simulate P shortage and depict the dose-response effect of two P supply levels. A variant without any additional P was included as control.

Nitrogen and potassium were added to all pots including the control at the beginning of the experiment as solutions of NH_4NO_3 and K_2SO_4, respectively, in optimal amounts for each species (Table 5, Table S1). Additional N and K supply was corrected for the CAT-extractable fractions in the growing medium, whereas N and K in the recycled fertilizers were negligible and thus not considered. It was assumed that CAT extraction determined the total nitrate N quantitatively and the easily exchangeable ammonium N and K fractions, and that these were all in plant-available form.

Table 4
Characterization of the growing medium.

Raw material	95% upland peat (H3-H8), clay granules, quartz sand, lime, NPK fertilizer; pH 5.8 ($CaCl_2$), salinity 1.2 g L^{-1} (KCl), EC 1875 µS cm^{-1}
Manufacturer	ASB Grünland GmbH, Germany
Nutrients (CAT)	mg L^{-1}
Nitrogen (N)	200
Phosphorus (P)	21.8
Potassium (K)	124.5
Magnesium (Mg)	100

CAT, extraction with calcium chloride and DTPA (diethylenetriaminepentaacetic acid).

Plants were pre-cultivated in germination trays without any additional fertilizer for two weeks before transplanting into prepared pots: sunflower and Chinese cabbage in 0.6 L pots of 12-cm diameter and marigold in 0.4 L pots of 10-cm diameter.

The pots were set up on tables in a greenhouse in a randomized complete block design with four replications and ten plants per replication, resulting in a total of 1560 pots for 39 treatments. The pots were irrigated from above following good horticultural practice, redundant water was allowed to drain from the pots. Additional lighting was provided during the first two weeks only. The air temperature in the greenhouse was approx. 26 °C during the day and 16 °C at night. Temperature was controlled by automatically opening windows. On days with very high light intensity, the greenhouse was automatically shaded. The sunflower and marigold were treated once against thrips with abamectin (Agrimec Pro, Syngenta Agro GmbH). Yellow and blue adhesive panels were hung up during the entire cultivation period to control whitefly and thrips. The Chinese cabbage pots were moved further apart twice in order to provide sufficient space for growth.

The marigold and sunflower were harvested once they had reached the flowering stage after 5 and 8 weeks, respectively. The Chinese cabbage was harvested after nine weeks. SPAD readings were carried out on cabbage (youngest fully developed leaf) using a Konica Minolta SPAD-502Plus. In all three plants, the shoots were cut 0.5 cm above the surface. The fully developed flowers of sunflower and marigold were counted and separated from the shoot, both weighed and then dried at 60 °C. Chinese cabbage leaves were counted and dried at 60 °C. Dry weight was determined and dry matter content calculated. Samples of the growing medium were taken from all pots individually before and after the experiment.

2.3. Sample analyses

The dried shoots and flowers were ground to approx. 1 mm in a cutting mill (SM200; Retsch GmbH, Haan, Germany). Concentration of P was determined using microwave digestion followed by ICP-OES measurement (DIN EN ISO 11885). Plant P content was calculated from dry matter yield and P concentration. The growing medium samples were dried at 105 °C,

Table 6
N and K concentrations in biomass and pH in growing medium of four treatments.

	Treatment	N in plant biomass mg (g DM)$^{-1}$	K in plant biomass mg (g DM)$^{-1}$	pH in growing medium
Sunflower shoots (without flowers)	P-Salt_manure	50.2	53.2	4.5
	Steam-dried solids	68.4	56.9	5.0
	TSP	59.4	55.6	4.6
	Control	69.8	52.2	4.5
Sunflower flowers	P-Salt_manure	71.3	30.9	Same pots as sunflower shoots
	Steam-dried solids	81.8	30.2	
	TSP	84.4	32.1	
	Control	87.5	29.0	
Chinese cabbage (whole plant)	P-Salt_manure	53.4	24.3	5.1
	Steam-dried solids	69.2	21.2	5.1
	TSP	50.1	21.6	5.1
	Control	68.2	20.2	5.2

sieved to 2 mm and then analysed for plant-available P (P(CAL)) using calcium-acetate-lactate extraction followed by flame photometer measurement (OENORM L 1087:2012-1). Unfortunately, the samples of marigold from the harvest date could not be analysed, as they were mislaid.

In order to ensure a sound experimental approach with comparable conditions in all pots and to ensure that side effects of other main plant nutrients are kept to a minimum, the N and K concentrations in sunflower and Chinese cabbage plants of four treatments were analysed (DIN EN 13654-2 and DIN EN ISO 11885, respectively). In addition, the pH was determined in the corresponding samples of growing media taken after harvest. Results (Table 6) showed that differences in N and K in plants and pH of medium between treatments were moderate and also did not reveal any clear pattern.

2.4. *Evaluation of synergistic effects and P use efficiency*

To evaluate the effects of the combined application of P-Salt_digestate and air-dried solids, theoretical biomass production was calculated from P-Salt_digestate and air-dried solids applied alone using the following equation:

$$\text{Theoretical biomass production} = (\text{Biomass yield}_{\text{P-Salt\_digestate}} + \text{Biomass yield}_{\text{air-dried solids}}) / 2 \quad (1)$$

where Biomass yield$_{\text{P-Salt_digestate}}$ is the biomass obtained with the application of P-Salt_digestate only and Biomass yield$_{\text{air-dried solids}}$ is the biomass obtained with the application of air-dried solids only.

Actually measured biomass yields that are higher than the calculated theoretical values indicate positive (synergistic) effects of the combined application and lower values indicate non-synergistic effects.

The P use efficiency was calculated using Equation [2] in order to compare the three species with regard to this parameter.

$$\text{P use efficiency} = ((\text{P content in fertilized plant} - \text{P content in untreated plant})/\text{P supply from fertilizer}) * 100 \quad (2)$$

2.5. *Statistical analysis*

Data analysis was performed using SAS software version 9.3 (SAS Institute Inc., Cary, NC, USA). Plant and growing medium data were subjected to a two-factor analysis of variance (ANOVA). Treatments and fertilization level were treated as fixed effects. Data were log-transformed where necessary. The graphs shown here were plotted with back-transformed data and simple means. Significance was determined at $P \leq 0.05$ using a multiple t-test, performed only on finding significant differences in the F-test. Significantly different means are indicated by different letters or mentioned in the text. The letters display the difference between marginal means of treatments across levels.

3. Results

3.1. *Sunflower*

The shoot biomass of sunflower was significantly higher in the treatments with TSP, steam-dried solids and the combination than in the control (Fig. 1). The flower biomass was higher for steam-dried solids than for TSP. There was no significant difference in flower biomass between TSP and the combination. By contrast, the shoot and flower biomass in the P-Salt treatments was comparable to that of the control. The two P-Salts performed similarly. The steam-dried solids induced significantly higher shoot and flower biomass than the air-dried solids. There were no relevant differences in shoot and flower biomass between the two fertilization levels. However, the number of

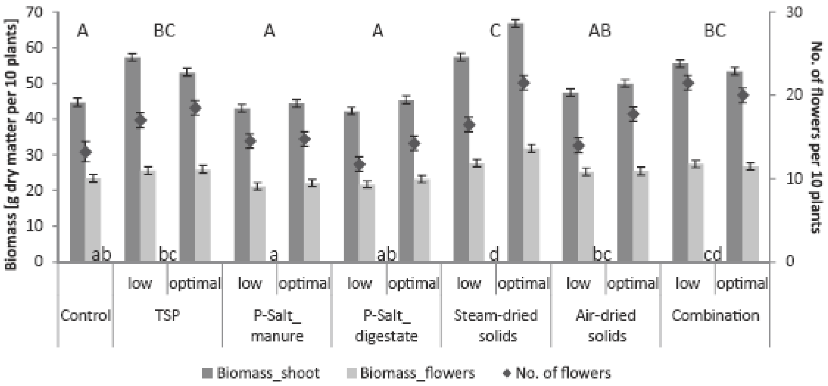

Fig. 1. Mean dry matter biomass of shoots (Biomass_shoot) and flowers (Biomass_flowers) and number of flowers of sunflower treated with P-Salts and dried solids compared to control and triple superphosphate (TSP). The error bars indicate pooled standard errors of the means; marginal means with identical letters are not significantly different from each other (upper-case for Biomass_shoot, lower-case for Biomass_flowers, $\alpha = 0.05$, $n = 4$) across the fertilization levels "low" and "optimal". For explanation of treatments, see 2.2.

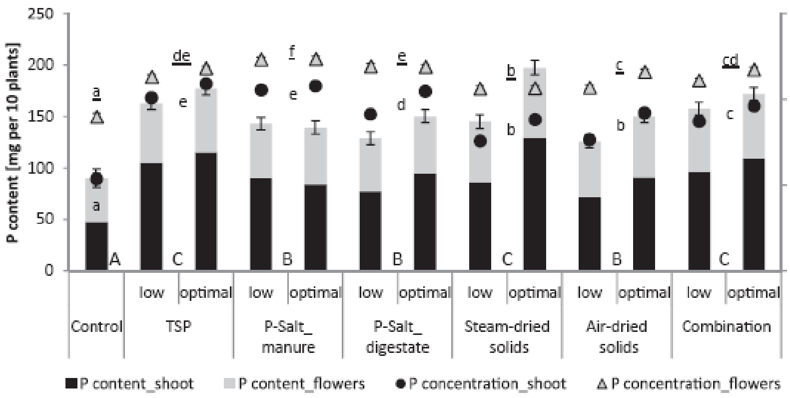

Fig. 2. P content and P concentration of sunflower shoots and flowers treated with P-Salts and dried solids compared to control and triple superphosphate (TSP). The error bars indicate pooled standard errors of the means; marginal means with identical letters are not significantly different from each other (upper-case for total P content (shoot + flower), lower-cases for shoot P concentration, underlined lower-case for flower P concentration, α = 0.05, n = 4) across the fertilization levels “low” and “optimal”. For explanation of treatments, see 2.2.

flowers per 10 plants was significantly higher for the optimal fertilizer level in most treatments than for the low level and the control (Fig. 1, significant differences not indicated). The highest number of flowers was observed in plants treated with steam-dried solids and the combination, followed by TSP and air-dried solids. The difference between air-dried solids and steam-dried solids was significant. The P-Salt treatments led to a similar number of flowers as the control.

The P content of sunflower was significantly increased by the application of TSP, steam-dried solids and the combination compared to the other treatments (Fig. 2). The difference between the P-Salts was not significant. However, the steam-dried solids resulted in significantly higher P contents than the air-dried solids. As expected, both fertilization levels led to significant differences in P content with highest values for the optimal level, followed by the low level and then the control.

The shoot P concentration was significantly higher in the treatments with P-Salt_manure and TSP compared to the other treatments (Fig. 2). The P-Salt_digestate treatment showed lower shoot P concentrations than P-Salt_manure, but performed better than the combination and the solids. There was no significant difference between steam-dried and air-dried solids here. The highest flower P concentration was found for P-Salt_manure, followed by P-Salt_digestate, TSP, the combination and the solids. The air-dried solids led to a higher flower P concentration than the steam-dried solids. The fertilization level significantly influenced the P concentration of both shoot and flower, with highest P values for the optimal P level and lowest for the control.

3.2. Marigold

Significant differences in shoot biomass production of marigold were only found between the treatments with manure-based P-Salt and air-dried solids (Fig. 3). The flower biomass did not differ from the control in any of the treatments (Fig. 3). The same applies to the number of flowers (between 1 and 10 flowers per 10 plants, data not shown).

Shoot P concentration of marigold was higher in all treatments than in the control. The highest concentration in absolute numbers was found in plants fertilized with TSP, followed by the P-Salts, the combination, the steam-dried and finally the air-dried solids. The shoot P concentration of plants treated with the combination was comparable to that of plants receiving P-Salts or steam-dried solids, but significantly higher than that of plants treated with air-dried solids (Fig. 4).

The flower P concentration showed a different pattern to that of shoot P concentration, but without any clear trend. The P-Salts and the solids led to significantly higher values than the control. The combination and TSP had results in between these values and that of the control (Fig. 4).

Total P contents of both P-Salt treatments, steam-dried solids and TSP were significantly higher than for air-dried solids and the control. Total P content of the combined treatment was only higher than the control (Fig. 4).

The fertilization level only influenced the P concentration in shoots and flowers ($P < 0.0001$). The shoot P concentration differed significantly between the two levels and the control, with highest values at the optimal level. The flower P concentration was higher at the optimal level than at the low level and the control.

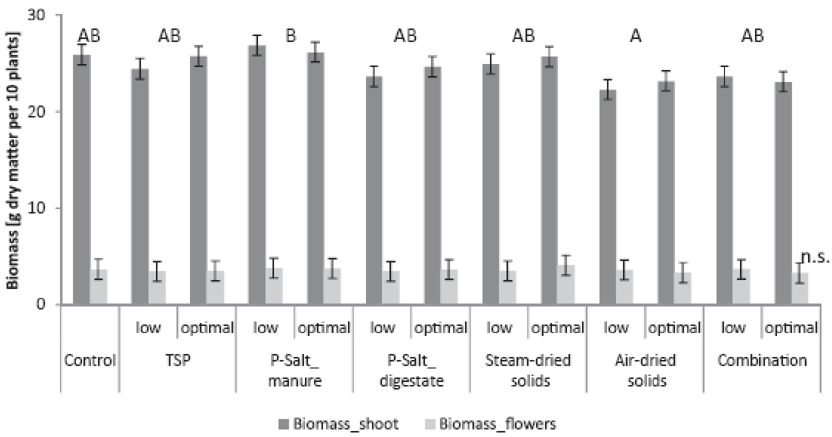

Fig. 3. Mean dry matter biomass production of shoots and flowers of marigold treated with P-Salts and dried solids compared to control and triple superphosphate (TSP). The error bars indicate pooled standard errors of the means; marginal means with identical letters are not significantly different from each other (upper-case for Biomass_shoot, not significant for Biomass_flowers, α = 0.05, n = 4) across the fertilization levels “low” and “optimal”. For explanation of treatments, see 2.2.

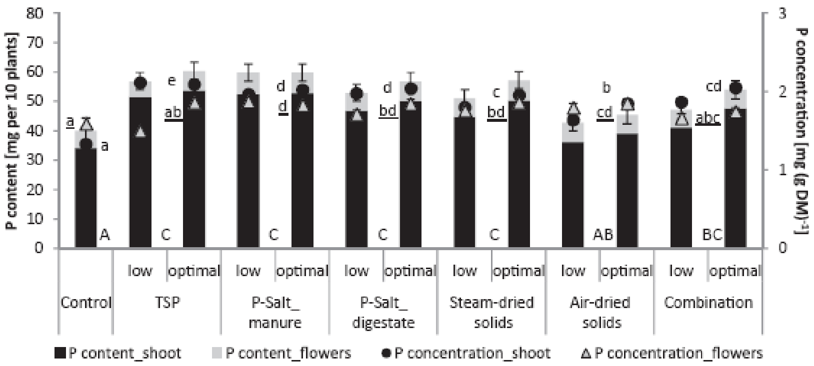

Fig. 4. P content and P concentration of marigold shoots and flowers treated with P-Salts and dried solids compared to control and triple superphosphate (TSP). The error bars indicate pooled standard errors of the means; marginal means with identical letters are not significantly different from each other (upper-case for total P content (shoot + flower), lower-case for shoot P concentration and underlined lower-case for flower P concentration, α = 0.05, n = 4) across the fertilization levels "low" and "optimal". For explanation of treatments, see 2.2.

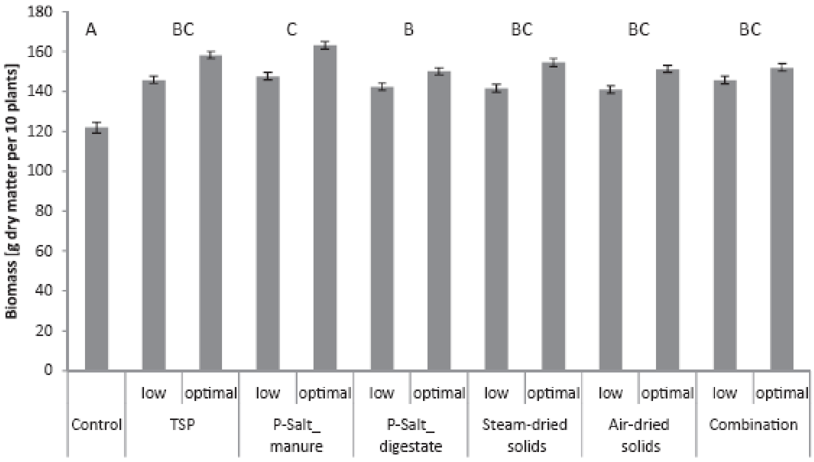

Fig. 5. Mean dry matter biomass production of Chinese cabbage treated with P-Salts and dried solids compared to control and triple superphosphate (TSP). The error bars indicate pooled standard errors of the means; marginal means with identical letters are not significantly different from each other (α = 0.05, n = 4) across the fertilization levels "low" and "optimal". For explanation of treatments, see 2.2.

3.3. *Chinese cabbage*

The dry matter yield of cabbage was significantly higher in all treatments than in the control. The highest DMY in absolute terms was found with manure-based P-Salt, yet this was only significantly different from the treatment with P-Salt_digestate (Fig. 5).

The highest P concentration was found in the cabbage plants treated with the two P-Salts and TSP, followed by the combination and both solids. The control had the lowest P concentration (Fig. 6).

The P content of the cabbage plants followed the same pattern as the P concentration (Fig. 6).

The fertilization level clearly influenced the DMY, P concentration and P content: all three variables were higher at the optimal level than at the low level and lowest in the control ($P < 0.0001$).

The number of leaves was significantly higher in all treatments than in the control (data not shown). Plants treated with the manure-based P-Salt developed the most leaves. In contrast, the highest SPAD readings were recorded for the leaves of the control plants, followed by the solids and then the other treatments, as was expected. Both parameters were significantly influenced by the fertilization level.

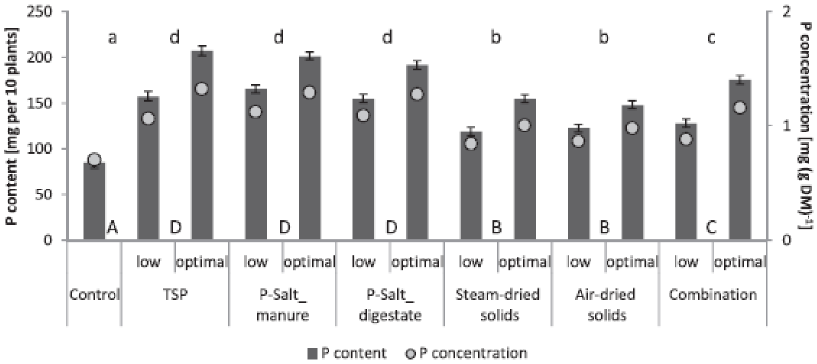

Fig. 6. P content and P concentration of Chinese cabbage treated with P-Salts and dried solids compared to control and triple superphosphate (TSP). The error bars indicate pooled standard errors of the means; marginal means with identical letters are not significantly different from each other (upper-case for P content, lower-case for P concentration, α = 0.05, n = 4) across the fertilization levels "low" and "optimal". For explanation of treatments, see 2.2.

Table 7
Evaluation of the synergistic effects of the combination treatment (P-Salt_digestate + air-dried solids). Theoretical biomass production was calculated using Equation 1 (Material and methods 2.4) and compared to the actual shoot and flower biomass in sunflower and marigold, and the actual total biomass in Chinese cabbage.

Plant species	Measurement	Combination			
		Low fertilization		Optimal fertilization	
		Shoot DM g per 10 plants	Flower DM	Shoot DM	Flower DM
Sunflower	Theoretical biomass production	44.81	23.49	47.70	24.35
	Biomass production measured	55.58	27.44	53.36	26.72
Marigold	Theoretical biomass production	22.96	3.57	23.89	3.51
	Biomass production measured	23.64	3.7	23.08	3.31
Chinese cabbage	Theoretical biomass production	141.69	–	150.59	–
	Biomass production measured	145.63	–	151.93	–

DM, dry matter.

3.4. Synergistic effects of the combined treatments

In sunflower, the actual shoot and flower biomass measured was higher than the theoretical biomass at both fertilization levels. In marigold, the same effect was visible, yet only for the low fertilization level. At the optimal level, the theoretical biomass was higher than the biomass measured. Chinese cabbage had higher actual biomass than theoretical biomass, at both fertilization levels (Table 7).

3.5. P use efficiency

The highest mean P use efficiency of the three crops was found in Chinese cabbage at 16% for the optimal and 19% for the low fertilization level. The percentages for sunflower (4% and 6% respectively) and marigold (2 and 3%), calculated for whole plants, were considerably lower (Table S2).

3.6. P concentration in growing medium

In sunflower, the highest P(CAL) contents at the beginning of the experiment were found in the pots fertilized with optimal levels of TSP and the P-Salts (Table 8). The P(CAL) contents in the treatments with P-Salt_digestate and both solids increased throughout the experiment. The P(CAL) was higher for steam-dried solids than for air-dried solids.

In Chinese cabbage, this was completely different. Here, the P(CAL) contents were higher at the beginning of the experiment than at the end in all treatments tested. The highest contents were found for the optimal levels of P-Salt_manure and the combination. The P(CAL) at the optimal level of P-Salt_manure (53.60 mg P (100 g medium)$^{-1}$) was considerably higher at the beginning of the experiment than at the optimal level of P-Salt_digestate (35.00 mg P (100 g medium)$^{-1}$).

For all treatments and all three crops, P(CAL) contents were mostly higher at the optimal levels than at the low levels.

4. Discussion

4.1. General comments

Overall, the yields and P concentrations of sunflower, marigold and Chinese cabbage observed in this study are comparable to the findings of related studies, including some using test soils low and high in P (Gunes et al., 2009).

In our study, the mean shoot P concentration of sunflower at 1.9 mg g^{-1} DM^{-1} can be seen as somewhat marginal (according to the classification by NSAC (2017) which rates P concentrations between 1.5 and 2.4 mg g^{-1} DM^{-1}as marginal), but not yet deficient. The NSAC classification levels refer to the top one to three most mature leaves collected at bud stage. Although we measured P in biomass of the entire shoot at flowering stage, our results seem comparable, as P concentration usually decreases over time. Vogel et al. (2015) tested struvite (magnesium ammonium phosphate) from wastewater compared to TSP in sunflower and found similar shoot P concentrations of 2.53 (struvite) and 2.11 mg g^{-1} DM^{-1} (TSP).

For marigold, the flower P concentration of all treated plants averaged 1.8 mg g^{-1} DM^{-1} in our study. A study by Naik (2015) found 2.6 mg P g^{-1} DM^{-1}, but the amount of P fertilizer was given on a per-hectare base and therefore not comparable. In contrast, Zeljković et al. (2013) found a much lower P concentration of only 0.53 mg P g^{-1} DM^{-1}in French marigold. Despite this low P concentration, which may be a consequence of lower P supply, they obtained biomass yields between 2.4–3.1 g DM per plant, which is comparable to those in our study.

In Chinese cabbage, the P concentration ranged from 0.84 mg g^{-1} DM^{-1}(steam-dried solids, low) to 1.32 mg g^{-1} DM^{-1}(TSP, high). Other studies have reported much higher values. For example, Li and Zhao (2003) found 5.2 mg g^{-1} DM^{-1}for struvite and 2.9 mg g^{-1} DM^{-1}for NP fertilizer and Ryu et al. (2012) found 5.4 mg g^{-1} DM^{-1}(struvite), 3.5 mg g^{-1} DM^{-1}(NPK fertilizer) and 1.8 mg g^{-1} DM^{-1}(compost). Chinese cabbage usually responds very sensitively to P deficiency.

Table 8
P(CAL) contents in the growing medium at the beginning and at the end of the experiment for the test crops and treatments.

		Control	TSP		P-Salt_ manure		P-Salt_ digestate		Steam-dried solids		Air-dried solids		Combination		LSD
			low	optimal	low	optimal	low	optimal	low	optimal	low	optimal	low	optimal	
		mg P (100 g medium)$^{-1}$													
Sunflower	start	15.20	63.80	122.80	73.60	120.80	70.20	131.80	31.80	48.60	21.60	33.20	64.80	80.00	–
	end	16.24	49.59	109.39	72.37	69.58	91.22	150.17	29.84	58.14	28.62	42.12	32.88	61.85	0.3993
Marigold	start	15.20	46.20	70.40	46.00	75.20	54.40	50.80	24.20	33.80	22.80	26.80	30.60	52.00	–
	end*	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Chinese cabbage	start	15.20	30.00	46.00	32.60	53.60	28.60	35.00	19.20	38.00	17.40	25.00	24.40	54.00	–
	end	10.02	15.74	17.39	14.27	15.52	17.64	18.99	13.17	14.87	14.32	13.47	11.62	16.12	0.3551

LSD, least significant difference.
* Samples from marigold were not analysed at the end of the experiment.

Symptoms include colour change to a greyish green or purple and small, possibly deformed leaves. As this was not observed in our study, it can be concluded that the P supply was sufficient, at least until the time of harvest. The mean P use efficiency of Chinese cabbage observed here was rather high at 16% for the optimal and 19% for the low fertilization level, particularly with regard to the limited cultivation time and compared to the other two species.

4.2. *Effect of P-Salts and solids on biomass production and P concentration*

4.2.1. *Steam-dried vs. air-dried solids*

The results showed that the steam-dried solids performed significantly better than the air-dried solids in terms of biomass in sunflower and Chinese cabbage. This trend was also seen to a certain extent in marigold, but was not significant. In sunflower and marigold, the P content of the biomass was also higher for the steam-dried than for the air-dried solids.

This effect of the steam-dried solids was not expected, as it was assumed that the higher drying temperature might negatively influence the P availability. In addition, the proportions of easily extractable $NaHCO_3$-soluble P were found to be lower in the steam-dried solids than in the air-dried solids. Nevertheless, the actual plant availability of P was higher in the steam-dried solids: fertilization with steam-dried solids led to higher P(CAL) contents in the growing medium in all three crops and at both levels than with air-dried solids, despite application of the same amount of total P.

The P solubility may have been altered during the steam drying process, either through the heat or possibly also through condensation on the surface of the solids. As steam is often used to increase the turnover and digestibility of organic matter (Hendriks and Zeeman, 2009), it may also have enhanced the release of P in this case by breaking down certain chemical compounds. The more P is released from the organic matter, the more is expected to be subsequently mineralized.

Fertilizer P can often be rapidly immobilized after application to the soil (Smit et al., 2009). The different drying conditions could also have affected the process of P immobilization after mixing the solids with the growing medium.

However, although highly energy-efficient, drying with superheated steam is not (yet) a standard technology and only makes sense if available on-site. Where this is not the case, the easier implementation of air-drying using waste heat may compensate for the lower fertilizing effect of the solids.

4.2.2. *Manure-based vs. digestate-based P-Salt*

The results of this study confirmed that differences in the performance of the two P-Salts are minimal. This is to be expected due to the similarities in the production processes and the chemical composition. Both P-Salts had comparably low proportions of P in easily extractable form. This was clearly visible despite the different analytical approaches used to characterize the P availability of the two P-Salts.

4.2.3. *P-Salts vs. TSP*

Positive effects of recycled fertilizers such as struvites and calcium phosphates have been reported in the literature for many different crop types. Vogel et al. (2015) found higher P uptake in sunflower treated with struvite than with TSP, and also increased biomass yield following both treatments compared to the control. The biomass P concentrations reported by Vogel et al. (2015) were comparable to those presented in our study. Ryu et al. (2012) found that Chinese cabbage had higher fresh and dry weight and P content when treated with struvite than with organic fertilizers. Li and Zhao (2003) reported that struvite precipitated from landfill leachate is a suitable fertilizer for fast-growing vegetables including Chinese flowering cabbage (*Brassica parachinensis*) and Chinese chard (*Brassica rapa* var. *chinensis*).

In our study, the biomass P content of marigold and Chinese cabbage was the same after application of P-Salts and TSP. However, it has not yet been clarified why these recycled salts are as efficient as they are, given that their P water solubility is usually very low compared to TSP. One of the main reasons for the efficient P uptake from the P-Salts was very likely the low pH of the growing medium (5.8). In addition, it has frequently been hypothesized that plants are able to make use of P with low plant availability – as provided by P-Salts – by changing the conditions in the rhizosphere through the release of organic acids (Jones, 1998; Hinsinger, 2001).

4.2.4. *P-Salts vs. solids*

The P content of the two ornamentals was comparable or higher in the treatment with steam-dried solids than with P-Salts.

The volume of fertilizer applied was much higher for the solids than for the P-Salts because the solids have a lower P concentration and higher fraction of organic matter. This high volume may have slightly increased and stabilized the low pH of the growing medium, more so for the steam-dried solids (pH 8.5) than for the air-dried solids (pH 7.1). This buffer effect of organic matter has frequently been observed (Bot and Benites, 2005).

The texture of the product groups may be another reason for the differences in P plant availability. Both P-Salts were finely ground powders in contrast to the coarse structure of the solids, which more resembled wood shavings. It is assumed that the P-Salts were able to supply P right from the beginning of the experiment, whereas P from solids had to be mineralized first. This becomes obvious from the analysis of the growing medium at the beginning of the experiment: samples from pots treated with solids had much lower P(CAL) contents than those treated with the P-Salts (Table 8). Thus, P-Salts seem more suitable for crops with high P demand and short growth period.

In contrast to the ornamentals, a slightly different performance of the P-Salts and solids was observed in Chinese cabbage. This was doubtlessly a consequence of the higher biomass growth. The supply of P in form of P-Salts seemed to be adequate for marigold, as it had the shortest cultivation period and the five weeks until harvest were possibly not sufficient for the P from the solids to be converted into a plant-available form. However, species with a longer cultivation period such as sunflower and Chinese cabbage can use the P slowly released from the solids. They develop more biomass and have an accompanying higher P demand, which can be met by the P-Salts or solids. The combination of both allows the P demand to be met in the short term (quickly available P from P-Salts) and in the long term (slowly released P from solids).

4.3. *The combination of P-Salt and separated solids has a synergistic effect on plant growth*

The comparison between the separate application of P-Salt_digestate and air-dried solids and their combination was included to clarify differences in fertilization effects (synergistic effects) and obtain information on the suitability of the combination of these recycled products as alternative P fertilizers. Currently, there are no comparable products or product combinations known which can be used for a direct comparison.

In our study, P-Salt_digestate was precipitated from the separated liquid fraction of biogas digestates (Bilbao et al., 2017) and then dried. It can be used separately or in combination with air-dried solids depending on the needs of the specific plant and the conditions of the soil or growing medium. This allows as much of the permanently accumulating biogas digestates as possible to be used - but in the form of a dried, storable and transportable product - and the nutrient cycle to be closed by returning nutrients and organic matter to the fields.

The precipitation of calcium or magnesium phosphates or struvite crystallization from various organic resources (Le Corre et al., 2009; Wilsenach et al., 2007; Greaves et al., 2010) is already well known and partly also in practice. Risberg et al. (2017), Brod et al. (2015) and

Holm-Nielsen et al. (2009) reported the generally positive effects of similar organic materials used as fertilizer, improving soil quality and decreasing the need for inorganic fertilizers with limited availability. In addition, several studies have examined the P fertilization effect of organic amendments, pointing out that they provide plants with more P than unfertilized controls (e.g. Waldrip et al., 2011; Requejo and Eichler-Löbermann, 2014; Duong et al., 2012). However, none of these organic materials were subjected to a drying or precipitation process as the products in our study were. Thus, the fertilizers in the cited studies had the disadvantage that they were neither storable for longer periods of time nor easy to handle and transport due to their high water content.

The positive effect of drying products with warm air is commonly used to advantage in the food industry (Pronyk et al., 2004), but as yet not for biogas digestates. Air-drying of solids from separated digestates or manure can also potentially reduce volume, moisture and unpleasant odours as well as stabilize the nutrient content of the separated solids.

In our study, it was observed that the steam-dried solids had an equivalent effect to TSP on plant biomass production in all tested plants. The effect of the digestate-based P-Salt was also similar to that of TSP in marigold and Chinese cabbage. However, the combination of the two had better effects (Table 6) than the separate fertilization with P-Salt or air-dried solids in all plants. The actual biomass production measured tended to be higher than the calculated theoretical biomass production, indicating synergistic effects of the combined application.

One possible reason for positive synergy effects of the combination treatment might be that the air-dried solids contributed positively to the moisture content in the medium and thus promoted the P solubility of the P-Salt by increasing water flow and improving P uptake in the plant.

This is in line with Vanden Nest et al. (2015) who found that the addition of separated solid digestates stimulates increases in soil P availability. In a review of numerous studies, Möller (2015) reported that digestate application at field level enhances soil microbial activity, but that these are short-term effects. It would appear that in a pot experiment with limited duration the air-dried solids can stimulate microbial biomass which then – as suggested by Olander and Vitousek (2000) – mobilizes additional P in the soil or medium through an increase in phosphatase activity. Thus, the P availability in the growing medium is increased and plant uptake facilitated.

In addition, the easily plant-available P fraction (Hedley fractionation) of the air-dried solids was low compared to that of the P-Salt, which may have promoted the enzyme activity and in turn increased the P availability and may also explain a stimulation of the microbial biomass. The negative feedback mechanism of enzyme activity, as described by Olander and Vitousek (2000), implies that enzyme activity is induced and nutrients are mineralized when nutrient supply is low. By contrast, when nutrient supply is high, the enzymes are suppressed and mineralization stops. This may explain the lower yields of plants treated with air-dried solids compared to the combination, because the enzymatic mineralization of P induced a lag phase. The combination treatment can compensate for this lag phase through the direct P fertilization effect of the P-Salt. The low P availability of the air-dried solids in the growing medium was also shown by the low P(CAL) contents throughout the experiment.The higher P(CAL) in the combination treatment during the entire experiment compared to air-dried solids applied alone was thus a result of the P-Salt_digestate. In sunflower for example, the treatment with P-Salt_digestate led to the generally highest P(CAL) contents. Another aspect to be considered is that mineral P is often inorganically immobilized. The application of the P-Salt (mineral P) together with the solids (organic P) might have caused an organic immobilization which was then followed by a slow remineralisation of P.

The higher pH of the P-Salt_digestate (8.3) and the air-dried solids (7.1) already mentioned might have also affected the structure of the growing medium and influenced P mobilization by increasing the pH in the medium to a range more optimal for P uptake.

As P is a major prerequisite for flowering quality and quantity, there is a particularly high demand for P in horticulture. The combination treatment tested in this study can supply flowering ornamentals with both direct and long-term fertilization, thus reducing the need for an additional P application during the cultivation time or even rendering it superfluous. This can also help reduce working hours and costs for personnel and material.

4.4. Recycled fertilizers enhance flowering in the same way as TSP and the level of P influences the number of flowers

In our study, effects of the recycled fertilizers and their different P application levels on flowering were visible for sunflower, but not for marigold. In sunflower, both P-Salts led to the lowest number of flowers, but to the highest P concentration levels in the flower biomass. A higher, similar number of flowers was obtained with air-dried solids and TSP. Steam-dried solids increased the number of flowers further, but both types of solids led to lower flower P concentrations than TSP. The combination induced the highest number of flowers of all treatments, with a higher flower P concentration than with TSP. Thus, the use of recycled fertilizers can definitely reduce the need for chemical fertilizers in the production of flowering plants without any flowering losses.

In sunflower, a higher P fertilization level led to both a higher number of flowers and an increase in flower P concentration, but in marigold the effect was not significant. However, both ornamentals had fully developed healthy flowers with no visible P deficiency symptoms, even at the low P level. Marigold was probably better adapted to the prevailling greenhouse conditions and the low P fertilization level may have been sufficient for the given cultivation period. Furthermore, the P demand of marigold was overall lower than that of sunflower, as it developed less biomass.

The relationship between P fertilization and flowering of greenhouse plants has been described in contradictory ways in the literature. On the one hand, an increased level of P has been reported to result in higher fresh and dry matter yield, number of flowers, plant height and concentration of essential oils in marigold (Negahban et al., 2014). Naik (2015) found that marigold plants receiving the highest level of P developed more flower heads per plant and had a significantly extended duration of full flowering. The results of Negahban et al. (2014) are in line with the findings of Anuradha et al. (1990), whereas those of Naik (2015) are not. On the other hand, Dahiya et al. (1998) reported a reduced number of flowers in marigold treated with P and Polara et al. (2015) did not find any influence of P on growth. Thus, the relationship between P fertilization and flower quantity has not yet been clearly demonstrated.

Bergmann (1993) has described a P concentration status between 2 and 5 mg g^{-1} DM^{-1} as optimal for flowering plants. However, a differentiation between marigold and sunflower needs to be made here. Sunflower produces larger and later flowers (usually one large main flower) than marigold (several, smaller flowers). Although marigold developed a higher number of flowers in our study, the flower biomass production was still higher in sunflower. As such, the P demand of sunflower can be expected to be higher as well. The importance of P fertilization for flowering in sunflower was clearly shown in our study, as the reduced P fertilization level resulted in a lower number of flowers.

Thus, we conclude that the P demand of ornamentals depends on the size and number of flowers as well as on the time of flowering. This applies not only to the amount of P but also to the timeframe of its fertilizing effect.

These findings also suggest that the fertilization level we defined as “optimal” for sunflower here may not actually be the optimal level. In addition, the chosen P fertilization levels seemed too similar to obtain a more distinct dose-response effect. The plant development status at the time of harvest was good and the P concentration indicated healthy plants with sufficient P supply. There were no recognisable symptoms of a lack of any macro- or micronutrients (pictures → supplementary material). However, it should be mentioned that the fertilization status measured at this point in time may not be adequate for a marketable sunflower plant, as it may display symptoms of deficiency shortly after sale.

As consumers - mostly hobby gardeners - are not familiar with plant care requirements, it is of particular importance for the producer to prevent the plants showing deficiency symptoms later on by supplying a certain nutrient reserve. This could be ensured by the combination treatment tested, as it resulted in the highest numbers of flowers with the highest P concentration levels. The long-term fertilization effect of the dried solids seen in this study suggests that these can secure P supply for several weeks and provide a positive medium structure and moisture in the pot. The differing P demand of flowering plants needs to be considered. Ornamentals that flower steadily for several weeks fulfill customers' expectations and render follow-up purchases more likely.

5. Conclusion

An instant, or at least fast, P uptake into plants is of particular importance in the horticultural sector, due to the short production periods in comparison to vegetable and field crops. The fertilizer needs to be applied in a form that ensures high P plant availability. In general, this requirement was met by all the recycled products tested, with the exception of the air-dried solids. The two P-Salts can be fully recommended as powerful P fertilizers for the horticultural sector. The combination of P-Salt and air-dried solids with its synergistic effect ensures short- and long-term P supply, and is thus particularly advantageous for the production of ornamentals marketed as potted plants because it guarantees long-term product quality. The two types of solid tested can fulfil two functions: as a source of P and/or as a component of growing media. For the purpose of P fertilization, the steam-dried solids are the better choice; the air-dried solids would need to be supplemented with additional P. As the solids had to be applied in rather high volumes, they could also serve as growing medium component or possibly as a peat substitute, or at least a supplement, in order to produce peat-reduced growing media. For this purpose, the air-dried solids are more suitable. Naturally, important quality parameters including pH and salt content should be continuously monitored. This would suggest that a simple solid-liquid separation of digestates or manure is sufficient in some cases. However, in others, advanced P recovery technologies are advantageous and urgently needed, for example in countries where P field application has been restricted (P could be removed and remaining material applied) and in regions with excess manure and digestate (could be separated into transportable salts, organic matter and water). In both examples, the P is removed and then used in other regions. The origin of the recycled products can also be seen as a marketing advantage. Substituting synthetic by organic products in ornamental production as well as in fertilizers and growing media for hobby gardeners may be appealing for environmentally conscious consumers.

In this study, we were able to show that recycling P by means of chemical and thermal processes has high potential in reducing the dependency of horticulture and agriculture on P fertilizers derived from phosphate rock. The recycled fertilizers were adaptable to the requirements of different types of ornamentals and met the P demand as efficiently as commercial phosphate fertilizer.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.scienta.2018.08.052.

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4 Efficiency of Recycled Biogas Digestates as Phosphorus Fertilizers for Maize

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Efficiency of Recycled Biogas Digestates as Phosphorus Fertilizers for Maize

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Abstract: Despite phosphorus resources on Earth being limited, over fertilization in many agricultural situations causes significant resource consumption. Phosphorus-recycling within agricultural production can reduce global dilution into the environment and is thus essential to secure sustainable future supply. This study investigated the fertilization efficacy of phosphorus fertilizers recycled from biogas digestates in maize shoots grown under controlled greenhouse conditions, in two soils, in a pot experiment. Variables investigated were plant-available phosphorus in soil, plant biomass production, and concentration of phosphorus, calcium, and magnesium in shoots. Soils were treated with three different fertilizer fractions, separated from biogas digestates, at equivalent phosphorus concentrations, using different combinations and application techniques, isolated or in combination, and compared to triple superphosphate (TSP) as a reference. One of the fractions (P-Salt) had effects on biomass production and plant phosphorus concentration equivalent to TSP in agricultural surface soil. In the second soil (with less active soil life and nutrient content), equivalence to TSP was achieved with combinations of two recycled fractions (P-Salt and dried solids). The enhancement of the phosphorus fertilizing effect by the solids was synergistic, indicating that the solids had a soil conditioning effect. The results show that biogas digestates are a valuable source for phosphorus recycling of fractions that have equivalent or even superior fertilizing properties compared to TSP.

Keywords: biogas digestates; recycled phosphorus fertilizer; phosphorus fertility indicators in soil; maize

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1. Introduction

One of the main factors increasing agricultural production is the use of organic and inorganic fertilizers. Phosphorus (P), an essential and irreplaceable element and fertilizer component, is a key factor for crop growth and quality [1]. Since exploitable P resources on Earth are limited and are, paradoxically, paired with systematic over fertilization with environmentally negative side effects, P-recycling from agricultural production is essential to secure future P supply for food production. Agriculture accounts for the consumption of approximately 80% of P from phosphate rock for fertilizer production [2]. Currently, the entire P for chemical fertilizers and feed is derived from P-rich rocks and about 70% of the known reserves are located in Morocco (Western Sahara) and China as the main exporters of P-ore [3]. Europe has no significant P mines and is highly dependent on the import of P [4]. Globally, the continued increase in population and changes in human diet will put further pressure on agricultural production to meet the growing food demand. Consequently, P is receiving more attention as a non-renewable resource [5,6]. These challenges stress the importance of finding alternative P sources in this century [7]. The requirements for alternative P-sources are multidimensional. Possible candidates must have similar characteristics compared to standard mineral fertilizers and would need to be available in large amounts with consistent quality and similar fertilization potential, as one unique characteristic of P is its low availability in soils due to its slow diffusion and high fixation [8].

One possibility to source additional P is from recycling biogas digestates that have valuable potential as organic fertilizer or soil amendment [9] and contain high amounts of plant nutrients, including N and P [10]. Agricultural biogas production is an efficient method of converting a wide range of organic waste into biogas, heat, and residual anaerobic digestates [11]. For example, animal manure slurries are co-fermented with energy crops like maize to produce biogas [12]. The boom of the European biogas production in recent years has been a consequence of the EU Commission's initiative to limit global climate change to two degrees Celsius by changing the European energy policy [13,14], which encouraged the use of renewable resources like energy crops and livestock effluents for biogas production. According to the European Biogas Association [15], the number and electrical capacity of biogas systems in European countries increased from 6227 plants with 4158 MW capacity in 2009 to more than 17,000 plants with over 9900 MW capacity in 2017. Especially in Germany, this has led to an increased production of biogas digestates of around 65.5 Million m^3 a^{-1} [9].

In regions with high livestock density and associated biogas production, the amounts of residual digestates are too high to be sustainably used locally without negative effects to the environment, and the handling of biogas digestates becomes an increasingly urgent and cost-intensive matter in terms of storage capacities and transport to arable farmland. Due to their high water content of around 90% [16], long-distance transport of raw digestates is neither profitable nor ecologically viable. In addition to other aspects like energy consumption, plant availability and adequate nutrient balance, one major objective of biogas digestate recycling must therefore be a drastic reduction of the water content. Due to a high proportion of organic P, plant availability of P in recovered products is often low or unpredictable, and the uptake in plants can differ substantially [17]. Johnston and Richards [18], as well as Römer [19], found that some P fertilizers from residues, such as wastewater or veal manure, ensured relatively good P availability, which indicates that the use of recycled P fertilizer in agriculture is possible.

The objective of a research project named GOBi (General Optimization of Biogas Processes) was the integral optimization of the biogas process chain to increase operational, material, energy and thereby ecological efficiency with special attention to the production of a natural, technically suitable fertilizer. As part of this, a new recycling technology for the recovery of P from biogas digestates was developed [20,21] to separate a salt containing struvite, calcium phosphate and magnesium phosphate (P-Salt) from the liquid fraction and to convert the solid digestate fraction into dried solids, resulting in nutrient-rich, storable and transportable fertilizer fractions for use as conventional fertilizers. The remaining aqueous phase was an N-rich liquid that could be used for plant irrigation without further processing. In summary, this new technology consisted of (a) mechanical separation of the digestate into a liquid and a solid phase, (b) solubilization of P from the liquid phase by addition of acid, followed by (c) precipitation of P from the liquid phase and (d) drying of the solid phase.

In the present study, the efficiency of recycled P-fertilizers, produced by the technology described above, was tested in a greenhouse pot experiment with maize plants in two different soil types, using conventional triple superphosphate (TSP) and untreated controls as reference. The first soil was a typical agricultural surface soil (0–10 cm) with active soil life and low nutrient P content compared to the second soil, a C-horizon (substratum) subsoil with less active soil life and low nutrient content, chosen as a model for less fertile soils. Maize was used as a representative, widely used input crop for biogas production. Especially at the beginning of plant growth, the P supply to maize plants is critical. *Zea mays* L. var. 'Carolinio' is a specific variety for the use as biogas substrate as it has a high dry matter yield potential. Dry matter was measured as an indicator of total biomass production of energy crops. The concentration and total content of P, Ca and Mg, as main components in the fertilizer fractions, was analyzed in plants as a measure for nutrient uptake, and calcium–acetate–lactate extraction of phosphorus (CAL-P) was analyzed as indicator for plant-available P in soil.

P adsorption to soil particles can be greatly reduced by co-application of organic substances [8]. Muhammad et al. [22] reported that combining mineral and organic fertilizers in the form of TSP and compost led to an increased plant P availability in a greenhouse experiment with maize. It could therefore be expected that a combination of both solid fractions, the dried organic solids and the precipitated P-Salt, might result in positive effects on fertilization and soil conditioning. Therefore, a second objective was to evaluate whether the combined application of P-Salt and a dried solid fraction in different ratios (1:1 or 1:2) might influence P fertilization. Different application techniques (pre-mixed in water suspension or dry-mixed) were used to get an indication for the robustness of the combined use in agricultural practice.

Digestate drying is a commercially available technology and according to the German Biogas Association [23] 500–700 dryers are in use in Germany's biogas industry [24]. Different drying techniques with advantages and disadvantages were discussed by Salamat et al. [24]. When using different temperatures (45 °C, 70 °C and 80 °C) for the air-drying process of the solids, no significant differences regarding organic dry matter and P were observed [25], whereas a pot experiment with dried sewage sludge resulted in a decreased P availability and P-uptake in barley plants [26]. Thus, as a third objective to assess differences between the drying processes of the previously separated solid fractions, solids from two drying processes (either with a warm-air dryer at 40 °C, or with a steam-dryer at 120 °C) were compared.

Based on the objectives described above, the following hypotheses were tested:

The P-Salt alone and combinations with solids recovered from the biogas digestate have fertilizer effects on plant dry matter, nutrient concentration and on CAL-P in soil, comparable to a mineral P fertilizer (TSP).

There is a synergetic effect between P-Salt and recycled solids (air-dried and steam-dried). This effect depends on the application technique (dry or suspended) and on the ratio of P-Salt to solid fractions.

Different drying procedures of the solids (air dried solids vs. steam dried solids) lead to different fertilization effects on maize plants.

2. Materials and Methods

The experimental part of this study was based on a greenhouse pot experiment with maize in two different soils to assess the P fertilizing effect of three recycled P-fertilizers and their different combinations, in comparison to the reference mineral fertilizer TSP and an unfertilized control.

2.1. Recycled P-Fertilizers

Recycled P-fertilizers were isolated from the anaerobic digestate of a biogas plant in Kupferzell, Germany [20]. A detailed overview about the process is given in Figure 1. In a first step, the digestate was mechanically separated into a solid and a liquid fraction. Phosphate salts (P-Salt) were solubilized from the liquid phase by acidification with H_2SO_4, followed by precipitation by increasing the pH with NaOH. The raw digestate contained sufficient magnesium (5.5% dry matter) to allow for struvite formation. However, the ammonium–N content (2.1% dry matter) was low, and therefore less than 50% was precipitated as struvite, whereas the rest was bound as calcium phosphates and magnesium phosphates. The resulting P-Salt fraction, a mixture of struvite, calcium phosphates and magnesium phosphates, was finally dried and powdered or granulated to give a homogeneous material for dosing and fertilization. The aqueous N-rich supernatant could directly be used for crop irrigation.

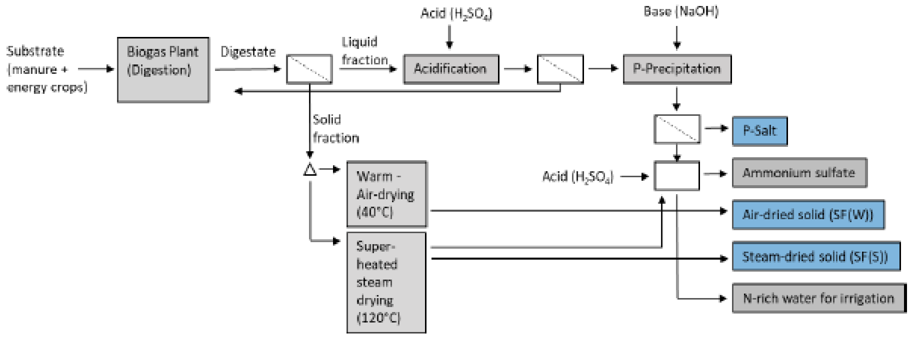

Figure 1. Overview of the recycling process of biogas digestates (according to [20]) to separate phosphate salts (P-Salts) from the liquid phase and to convert the solid digestate fraction into dried solids (SF (W/S) (blue boxes). All rights on this recycling process belongs to Fraunhofer IGB, Stuttgart, Germany [21].

From the solid fraction of the digestate, two types of dried solids were recovered, produced by drying to approximately 90% dry matter (DM) with either a warm-air dryer at 40 °C (air-dried separated solids, "SF(W)") or a steam-dryer at 120 °C (steam-dried separated solids, "SF(S)"). The measured P content of the different fertilizer fractions is given in Table 1. Total water-soluble P was determined by extraction with water followed by ammonium-citrate and analysis by ICP-OES according to VDLUFA II 4.1.4 [27]. A characterization of the different P forms in the recycled P fertilizers was performed using a modified Hedley-fractionation method [28,29]—for details see Wollmann et al. [30]. P, Mg, Ca, Na, K and Fe were measured using ICP-OES with HNO_3 extraction (DIN EN ISO 11885). Ammonium–N was determined by DIN 38406-E5.

Table 1. Characteristics of phosphate salt (P-Salt) and solids.

Property/Variable	P-Salt (Precipitated from Liquid Digestate Fraction)	Steam-Dried Solids (Separated from Solid Digestate Fraction, Dried at 120 °C)	Air-Dried Solids (Separated from Solid Digestate Fraction, Dried at 40 °C)	Mineral TSP (Triple-Superphosphate, P Fertilizer as Reference)
Abbreviation	P-Salt	SF (S)	SF (W)	TSP
DM [% FM]	69.7	91.6	95.4	
Pt [% DM]	11.3	2.3	2.1	19.0
Water soluble P [% DM]	0.13	0.35	0.35	
Sequentially fractionated with … in (mg P (g DM)$^{-1}$)				
$NaHCO_3$ (easily available P)	29.9	6.7	7.5	
NaOH	6.3	0.98	1.3	
H_2SO_4 (sparingly available P)	53.3	0.96	1.74	
pH [$CaCl_2$]	8.3	8.5	7.1	
Ca [% DM]	8.2	1.8	1.7	15.0
Mg [% DM]	5.5	0.5	0.5	
K [% DM]	1.1	1.6	1.8	
Na [% DM]	0.43	0.07	0.08	
Fe [% DM]	0.55	0.13	0.14	
Ammonium N (NH_4-N) [% DM]	2.1	1.4	1.5	

Dry matter (DM) in % fresh matter (FM), total P (P_t) content in % of DM, water soluble P in % DM and P contained in different fractions of sequentially extracted P ($NaHCO_3$, NaOH, H_2SO_4), indicated as total amounts (mg P (g DM)$^{-1}$) and pH in $CaCl_2$ and total Ca, Mg, K, Na, Fe and N in % DM of the investigated fertilizers P-Salt, SF (S) and SF (W) and the reference TSP; all% in (w/w). P_t determined with dried fertilizers and aqua regia extraction, according to VDLUFA (2000) and measured with ICP-OES.

2.2. Soil Characteristics

The pot experiments were carried out using two soils, namely a silty loam and a clay loam, both selected for their low concentration of CAL-P, defined as P extractable in calcium–acetate–lactate, according to [31]. The silty loam was a subsoil collected at the research station Kleinhohenheim of the University of Hohenheim, Germany, with low fertility and low microbial activity and thus not a typical, representative agricultural soil, but selected to show influences of low microbiological activity on fertilizer efficacy. The clay loam was an agricultural surface soil with high active soil life, high water retention capacity and was collected from agricultural soil in Kleinansbach, Germany.

2.3. *Soil Sampling and Analysis of P, K, Mg, C_{org}, N_t and pH*

Soil samples were taken from each pot both before maize sowing and after harvest. Samples were stored at −20 °C until analysis. Plant available P in soil (dried at 105 °C and sieved to 2 mm) was analyzed using the CAL extraction method (calcium–acetate–lactate extractable P, [31]). The same method was used for K and Mg determination. C and N contents were determined with a CN analyzer (VarioMax, Elementar Analysensysteme, Hanau, Germany). Soil pH was measured in 0.01 M $CaCl_2$ suspension [32].

2.4. *Fertilizer Dosing*

All P-fertilizers and their combinations were applied once at the beginning of the experiment to soil at a dose equivalent to 150 mg total P per kg soil (standard dose for P supply) prior to sowing of maize. In addition to the three isolated P fertilizer fractions, combinations were tested with P-Salt combined with SF (W) or SF (S) in the ratios of 1:1 or 1:2. The corresponding dose weights of single doses or combinations were calculated from actually measured P concentrations in the used fertilizer fractions. For combined fertilizers, a ratio of 1:1 means that 75 mg total P per kg soil came from the P-Salt and 75 mg total P per kg soil came from the separated solid fraction, amounting to 150 mg total P per kg soil. Accordingly, combinations of 1:2 were generated by mixing 50 mg total P per kg soil coming from the solid fraction with 100 mg total P per kg soil coming from the P-Salt. Simultaneous or sequential application was chosen in order to test P-availability effects depending on the application technique. "Dry" application was done by homogeneously mixing both components into the soil sequentially (first P-Salt, followed by SF (S/W)). For the "suspended" application, both components were first mixed together with water in a separate vessel before adding and mixing it as one product into the soil.

2.5. *Experimental Details*

Fertilization doses of the three different recycled P-fertilizers, the eight different fertilizer combinations and variants of them, as well as the reference fertilizer TSP, were given at equimolar P amounts per pot. The corresponding dose weights of single doses or combinations were calculated from P concentrations in the used fertilizer fractions pre-measured by ICP-OES (extraction with HNO_3). The required amounts of P-Salt, SF (W) and SF (S) and their different combinations were homogeneously mixed with 3 kg soil (dry weight) and filled into round plastic pots (4 liter volume, 20 cm diameter). The conventional fertilizer TSP was pre-mixed with deionized (DI) water to ensure the exact dosage of the small amounts and then added to the soil. Additional mineral fertilizer (ammonium nitrate (NH_4NO_3), potassium sulfate (K_2SO_4), magnesium sulfate ($MgSO_4$), Fe–Sequestren (Ferric EDTA)) was added once to each pot, including the untreated controls. After fertilization, the soil was mixed, watered to a water-holding capacity (WHC) of 70% and incubated for two days in the greenhouse at 24 °C before sowing the maize seeds into the soil. The commercially used biogas crop *Zea mays* L. var. Carolinio (KWS SAAT SE & Co. KGaA, Einbeck, Germany) was used. Three seeds were sown per pot into the soil at a 4-cm depth. After germination, the number of seedlings per pot was reduced to one plant per pot. A second additional mineral fertilization event, only with N, was applied three weeks after germination. During the experiment, each pot was weight-controlled every three days and irrigated with deionized water to maintain a water content of 70% water holding capacity (WHC). A detailed overview of the conditions is included in Table 2 and in Figure 2.

Table 2. Experimental setup of the greenhouse pot experiments.

Crop	Maize (*Zea mays* L. var. Carolinio), 3 seeds per pot; after germination reduction to 1 seedling per pot
Soil	Silty loam: Texture uL; pH [$CaCl_2$] 7.3; nutrient status for P, K, Mg (all CAL) in mg/kg soil: 7; 71; 210; C_{org}%: 0.3; N_t%: 0.04 Clay loam: Texture tL; pH [$CaCl_2$] 7.4; nutrient status for P, K, Mg (all CAL) in (mg (kg soil)$^{-1}$): 26; 150; 580; C_{org}%: 3.6; N_t%: 0.24
Additional mineral fertilization per pot (excluding P)	Before sowing: 200 (mg N (kg soil)$^{-1}$) as NH_4NO_3, 200 (mg K (kg soil)$^{-1}$) as K_2SO_4, 100 (mg Mg (kg soil)$^{-1}$) as $MgSO_4{\cdot}7H_2O$ and 10 (mg (kg soil)$^{-1}$) Fe–Sequestren (6%) 4 weeks after sowing: 200 (mg N (kg soil)$^{-1}$) as NH_4NO_3
Experimental Duration	Total: 50 days
Conditions	ambient greenhouse conditions (University of Hohenheim, Germany, June 2016), ca. 16 h light, 8 h dark, ca. 20 °C; initial watering to 70% water-holding capacity (WHC) with deionized (DI) water, additional watering when required (weight control every 2–3 days)
P-fertilizer treatments	
Recycled P-fertilizers	**all mg below refers to P equivalents per 1 kg dry soil**
P-Salt SF (W) SF (S)	150 mg 150 mg 150 mg
SF (W) + P-Salt (1:1)	Dry mixed (dry): 75 mg SF (W) mixed into the soil, directly followed by 75 mg P-Salt mixed into the soil Suspended mixed (susp.): 75 mg SF (W) + 75 mg P-Salt + 50 mL DI water, pre-suspended in a separate vessel before mixing into soil
SF (W) + P-Salt (1:2)	Dry mixed (dry): 50 mg SF (W) mixed into the soil, directly followed by 100 mg P-Salt mixed into the soil Suspended mixed (susp.): 50 mg SF (W) + 100 mg P-Salt + 50 mL DI water, pre-suspended in a separate vessel before mixing into soil
SF(S) + P-Salt (1:1)	Dry mixed (dry): 75 mg SF (S) mixed into the soil, directly followed by 75 mg P-Salt mixed into the soil Suspended mixed (susp.): 75 mg SF (S) + 75 mg P-Salt + 50 mL DI water, pre-suspended in a separate vessel before mixing into soil
SF(S) + P-Salt (1:2)	Dry mixed (dry): 50 mg SF (S) mixed into the soil, directly followed by 100 mg P-Salt mixed into the soil Suspended mixed (susp.): 50 mg SF (S) + 100 mg P-Salt + 50 mL DI water, pre-suspended in a separate vessel before mixing into soil
Control treatments Triple superphosphate (TSP) Negative control	 Positive reference; 150 mg DI water

The pots were set up in a randomized complete block design on tables in the same greenhouse, using four replicates per treatment, resulting in a total of 104 pots, 52 for each soil type. C_{org} = organic carbon; N_t = total nitrogen.

2.6. Maize Harvest and P, Mg and Ca Analysis

After 50 days, the maize shoots were cut 0.5 cm above the soil surface, and fresh weight and dry weight (after drying at 60 °C for 48 h, dry matter, DM) were recorded. Analyses were carried out after microwave extraction [33] using ICP-OES (Agilent 5100, Santa Clara, CA, USA) according to DIN EN ISO 11885: dried plant material was ground using a laboratory disk mill (TS 250, Siebtechnik GmbH, Mülheim and der Ruhr, Germany) and 0.5 g of the plant material was suspended in concentrated HNO_3 and H_2O_2, followed by microwave extraction at 210 °C for 62 min and filtration. Shoot nutrient (P, Mg Ca) content was calculated as mg/shoot and as mg/shoot DM.

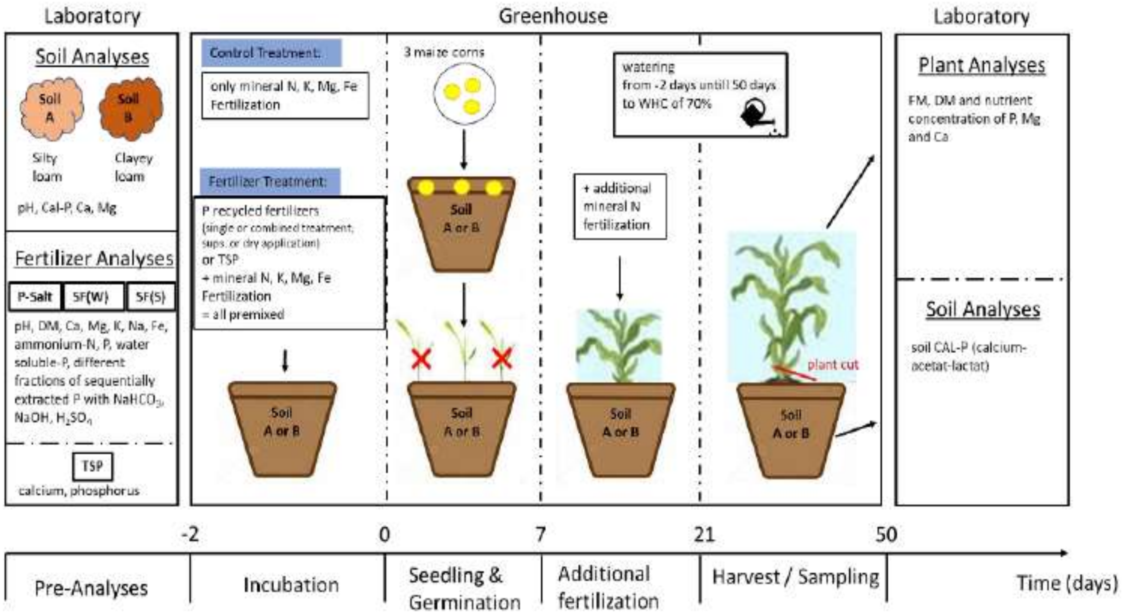

Figure 2. Overview of the experimental set-up of the greenhouse pot experiment with maize. Fertilizer fractions tested were P-Salt (P-enriched precipitate from the liquid fraction), SF (W) (air-dried solid fraction), SF(S) (steam-dried solid fraction), and different combinations of them, compared to unfertilized control and triple superphosphate (TSP). Maize plants were cultivated for 50 days in a silty loam and clay loam soil. DM—dry matter; FM—fresh matter; Ca—calcium; Mg—magnesium; K—potassium; N—nitrogen; Fe—iron; WHC—water holding capacity.

2.7. Evaluation of Synergistic Effects

In order to evaluate the effects of the combined application of P-Salt + SF (SF (W) or SF (S)), theoretical biomass production and P content was calculated from P-Salt and SF applied alone using the following equation:

Calculated DM yield for ratio 1:1 (Equation (1)) and 1:2 (Equation (2)):

$$\text{calculated DM yield} = \frac{\text{SF (W or S) DM yield} + \text{P} - \text{Salt DM yield}}{2} \quad (1)$$

$$\text{calculated DM yield} = \frac{\text{SF (W or S) DM yield} + (\text{P} - \text{Salt DM yield}) \times 2}{3} \quad (2)$$

Calculated P content for ratio 1:1 (Equation (3)) and 1:2 (Equation (4)):

$$\text{calculated P content} = \frac{(\text{SF (W or S) P content} + \text{P} - \text{Salt P content})}{2} \quad (3)$$

$$\text{calculated P content} = \frac{\text{SF (W or S)P content} + (\text{P} - \text{Salt P content}) \times 2}{3} \quad (4)$$

Measured values higher than the calculated values after combined application were interpreted as synergistic effects, whereas measured values equal to or lower than the calculated ones indicated non-synergistic effects.

2.8. Statistical Analysis

Data analysis was performed using the statistical computing software R version 4.0.4. A block design setup with fertilizer treatments and soil types as fixed elements and different variables (P concentration, DM yield and P content in the maize plants and CAL-P in soils) was assessed using a two-factorial linear model ($n = 4$).

The model can be described as follows:

$$y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + b_k + e_{ijk},$$

where y_{ijk} is the yield (or CAL-P or P-concentration) of the ith fertilizer and jth soil type in kth block, μ is the general mean, α_i is the main effect of ith fertilizer, β_j the main effect of jth soil type, $(\alpha\beta)_{ij}$ the fertilizer-by-soil type interaction, b_k the effect of kth block, and e_{ijk} is the residual error. Fertilizers and soils were treated as fixed elements.

Data were log-transformed in order to meet the model assumption of normality of residuals and variance homogeneity, when necessary. Least square means and letter display for pairwise comparison were performed using the R packages emmeans [34] and multcomp [35,36]. Significance was determined at $p \leq 0.05$ using a Tukey's test, performed only on finding significant differences in the F-test. Significantly different mean values were indicated by different letters and mentioned in the text. Lowercase vs. uppercase letters were used to indicate significant differences between both soils within the same treatments, so that, e.g., the use of capital letters (regardless which one) in both soils indicates non-significance between the same treatments.

3. Results

3.1. Effect of P-Fertilizers on Biomass Yield and Plant Nutrient Concentration

Maize shoot dry matter yield (DM yield) is shown in Figure 3. In the silty loam soil (nutrient-poor subsoil, low active soil life), untreated controls had the lowest DM yield (0.9 g/plant) compared to all fertilizer treatments. When dosed alone, the increase was highest with SF (S), at a level equivalent to TSP. The recovered P-Salt alone had the lowest effect of all applied fertilizers. The highest DM yields (10.0 g/plant) were detected when SF (W or S) and P-Salt fractions were combined, in some combinations with significantly higher DM compared to the reference TSP. All combination treatments (SF + P-Salt) resulted in much higher DM yield than theoretically calculated from the single components' yields, indicating a synergistic effect between both fractions. Combinations of air-dried solids (SF(W)) with P-Salt led to higher DM yields when dosed separately, whereas those with steam-dried solids (SF (S)) gave higher DM yield when given as mixture. Mixtures with high SF(W/S) fraction content (1:1) had a higher DM yield than combinations with higher P-Salt content (1:2). Nevertheless, even the (1:2) combination of P-Salt with air-dried solids (SF(W) (applied dry) resulted in DM yield comparable to the reference TSP.

Plants grown in the clay loam soil (nutrient-rich surface soil, high active soil life) already developed a level of 5.9 g DM/plant in untreated controls, which was in the order of magnitude of the nutrient-poor subsoil after fertilization. The TSP reference dosing increased DM by only a factor of ca. 2 to 12.4 g/plant. In contrast to the silty loam, single dosing of P-Salt here had the highest effect of all treatments (14.69 mg DM yield/plant), even higher than the reference TSP. Similar to the silty loam, steam-dried solids (SF (S)) alone gave higher yields than air-dried solids (SF(W)). All combinations of the recycled fertilizer fractions were on the same order of magnitude as the TSP control. Higher P-Salt content in the combinations and SF(S) rather than SF(W) resulted in slightly higher yield. Combinations generally resulted in higher DM yield when dosed dry, however differences were less pronounced than in the silty loam. A comparison of the yields calculated from single dosing with those of the combinations showed little, mostly insignificant differences, indicating additive effects of both fraction types in this case. Overall, all treatments and combinations resulted in a significant increase of plant dry matter levels compared to untreated controls, and for both soils combinations of the recycled fertilizers were identified that gave equivalent or even higher yield than the reference TSP.

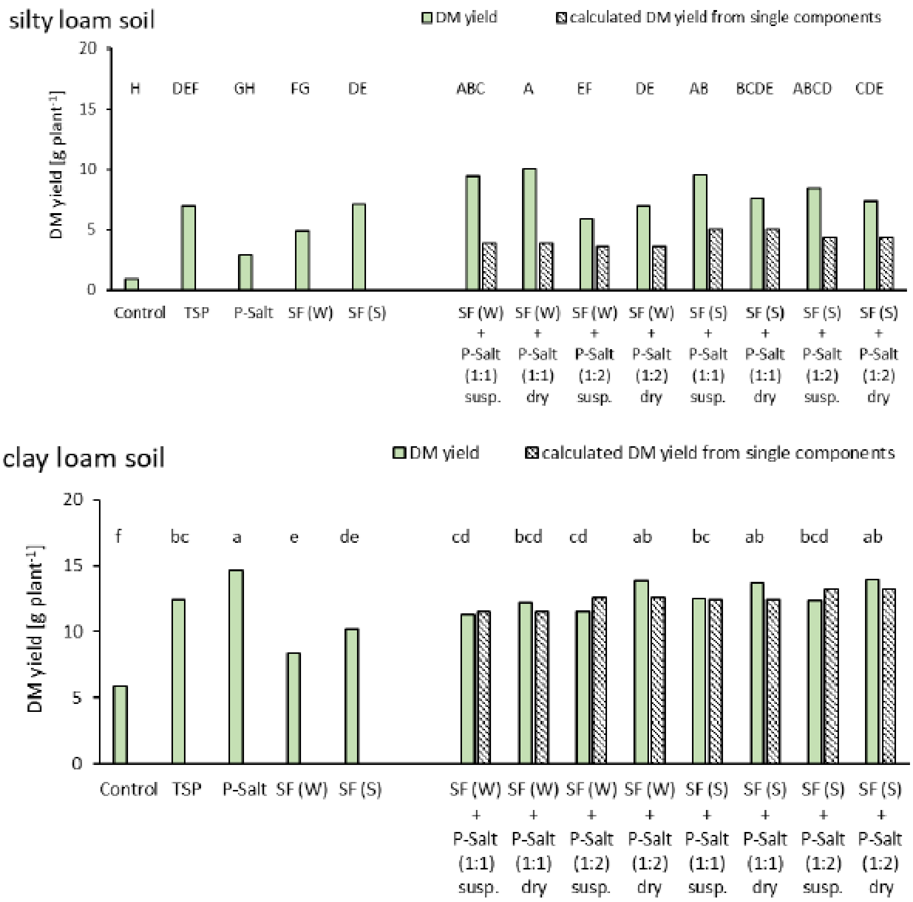

Figure 3. Mean shoot dry matter yield of maize (DM yield) in g plant^{-1} after soil treatment with different recycled digestate fertilizers in a total dose equivalent to 150 mg P (kg soil^{-1}). Fertilizer fractions tested were P-Salt (P-enriched precipitate from the liquid fraction), SF (W) (air-dried solid fraction), SF(S) (steam-dried solid fraction), and different combinations of them, compared to unfertilized control and triple superphosphate (TSP). Maize plants were cultivated for 50 days in a silty loam and clay loam soil. Based on the total fertilizer dose corresponding to 150 mg P (kg soil^{-1}), designation 1:1 means that fertilizers were applied with a mass portion of SF (W or S) containing 75 mg P (kg soil^{-1}) + a mass portion of P-Salt containing 75 mg P (kg soil^{-1}); likewise, 1:2 means using a mass of SF (W or S) with 50 mg (kg soil^{-1}) + a mass of P-Salt with 100 mg (kg soil^{-1}). The application technique "susp." (suspended) describes that both components were pre-mixed and homogenized with 50 mL water in a vessel before being homogenized into the soil; "dry" means that the solid fraction SF was first mixed into the soil followed by the P-Salt, both without water. "Calculated DM yield from single components" represent a mathematical calculation of the combinations based on the results of the measured DM yield of each single component (P-Salt, SF(W), SF(S)) to indicate possible additive effects (material and methods: evaluation of synergistic effects Equations (1) and (2)). Data are means of four replicates each. Different letters denote significant differences (two-factorial Tukey's test with $p \leq 0.05$). Lowercase letters for the clay loam indicate that, in this case, all treatment groups were significantly different from those of the silty loam with the same treatment.

Figure 4 summarizes the nutrient concentration in mg/g DM of P, Ca and Mg in the maize shoots after harvest, as an indicator for nutrient net uptake into the plants. The P concentration in the maize shoots grown in the silty loam soil increased significantly with all fertilizer combinations and especially after treatment with P-Salt alone (10.9 mg/g DM), a combination of dry applied SF (S) + P-Salt (1:2) (5.4 mg/g DM) and SF (W) + P-Salt (1:2) (4.8 mg/g DM). These three applications resulted in much higher P concentrations in the plants compared to the reference TSP (1.9 mg/g DM), indicating that P-mobilization from P-Salt was higher compared to TSP in this nutrient-poor soil. In contrast, the lowest, but still significant effect on P-concentration in the shoots, compared to untreated controls, was detected after single application of the solid fractions (SF (W/S) where the P-concentration was low (Table 1). In a comparison of the application technique of the combined fertilizer treatments (dry or suspended), dry application consistently resulted in much higher P concentrations compared to suspended application, especially when the ratio SF(W/S) + P-Salt was high (1:2). Even at a ratio of 1:1, higher P concentrations in the shoots were found in all dry applications compared to suspended applications. The lowest P-concentration in the shoots (2.1 mg/g DM) was found with a 1:1 suspended mixture of SF (W) + P-Salt, still significantly higher than untreated controls and not significantly different from treatment with the reference TSP.

Ca and Mg-concentration per maize plant were evaluated to monitor the influence of the P-Salt on the net-uptake of both nutrients in plants. The highest Ca concentration in the maize shoots after harvest was found in the untreated controls with 20.7 mg/g DM. All other treatments had much lower concentrations between 5.0 mg/g DM (SF(S) + P-Salt (1:1), dry) and 7.6 mg/g DM (P-Salt). Similar Ca concentrations were detected in the treatments with TSP, P-Salt and SF(W) with a single application. Combined fertilizer treatments resulted in slightly lower Ca concentrations, with a tendency of slightly higher values for higher P-Salt ratios (1:2) and using the suspended application technique vs. dry application. Overall, however, only low differences between all treatment groups were observed. The Mg concentration, like the Ca concentration, was highest in the untreated control plants (10.4 mg/g DM). All single and combined fertilizer treatments resulted in Mg concentrations of 4–5 mg/g DM, with no or only small significant differences between them. The only exception was P-Salt alone with an elevated concentration of 7.3 mg/g DM.

In the clay loam soil, the P concentration in dried maize shoots did not differ significantly between the fertilizer scenarios, even including the untreated control. None of the treatments apparently lead to an increase of P-concentration in the plants, all with levels around 2 mg/g DM. Likewise, the Ca concentration in maize shoots was undistinguishable between the fertilizer scenarios and the control. The Mg concentrations in the maize shoots resulted in concentration levels between 3.5 and 5.5 mg/g DM, with the highest value (5.5 mg/g DM) after P-Salt treatment. Only a slight tendency to lower values was detected with the combination treatments, with higher P-Salt ratios (1:2) leading to higher Mg content.

3.2. *Effect of P-Fertilizers on Plant Nutrient Content*

For a comparison of the total net uptake of P, Ca and Mg per plant, the data in Figure 4 were re-evaluated as total content per plant (Figure 5). Similar to the dry matter results, the theoretical P content calculated for the combination treatments from the addition of the values of the single components was compared to the measured values to evaluate synergistic effects (material and methods: evaluation of synergistic effects Equations (3) and (4)).

Compared to the untreated controls, the total P-content per plant increased with all applied P fertilizers in the silty loam. Compared to TSP, combinations of the recycled fertilizers had similar or higher effects on P-content, with a slightly higher effect of SF(S) vs. SF (W). Differences between the application techniques were clearly visible for all fertilizer combination in favor of higher P-contents after dry application of the fractions. Furthermore, with dry application, the fertilizer ratio (1:2) caused higher P-contents compared to the ratio (1:1). Especially, the SF(S) + P-Salt (1:2) dry application showed highest total P-net-uptake per plant across all treatments. All combination treatments (SF + P-Salt), except for SF(W/S) + P-Salt (1:2) suspended, resulted in much higher P-contents than theoretically calculated from the single components' P-contents, indicating a synergistic effect between both fractions. The Ca-content per plant was increased by all fertilizer treatments compared to the control, with highest Ca-content for combination treatments, namely SF(W) + P-Salt (1:1) suspended and dry and the combination SF(S) + P-Salt (1:1) suspended. Compared to TSP, the other fertilizer treatments resulted in similar or lower Ca- contents with the lowest Ca-content of the fertilizer treatments of P-Salt alone. The single solids resulted in slightly higher Ca-contents, with increased Ca-contents with SF(S) single treatment. Comparing the fertilizer treatments, the higher P-Salt ratio of 1:2 and the dry application technique had decreasing effects on Ca-content in those combinations with SF(W). For the SF(S) combinations, only decreasing effects on Ca-content with the dry application technique was observed. For Mg-content, all fertilizer combinations resulted in higher Mg-contents compared to the single fertilizer application and the reference TSP. Similar to Ca, the highest Mg- contents per plant were observed in the SF(W) + P-Salt (1:1) suspended and dry, whereas a higher P-Salt ratio (1:2) decreased the Mg-content. The SF(S) + P-Salt combinations resulted in slightly lower Mg-contents with no different effects between both ratios and different application techniques. No differences between single fertilizers P-Salt and SF(W) were observed, whereas SF(S) was slightly increased compared to SF(W). Compared to the reference TSP, all three single components resulted in lower Mg-contents.

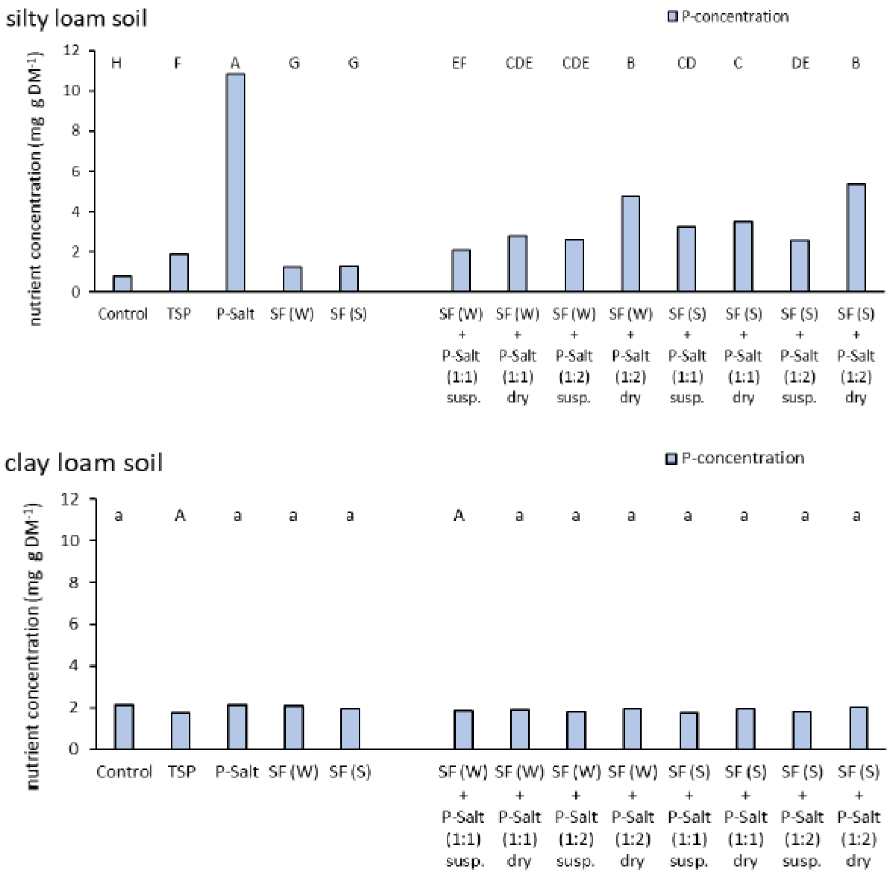

Figure 4. *Cont.*

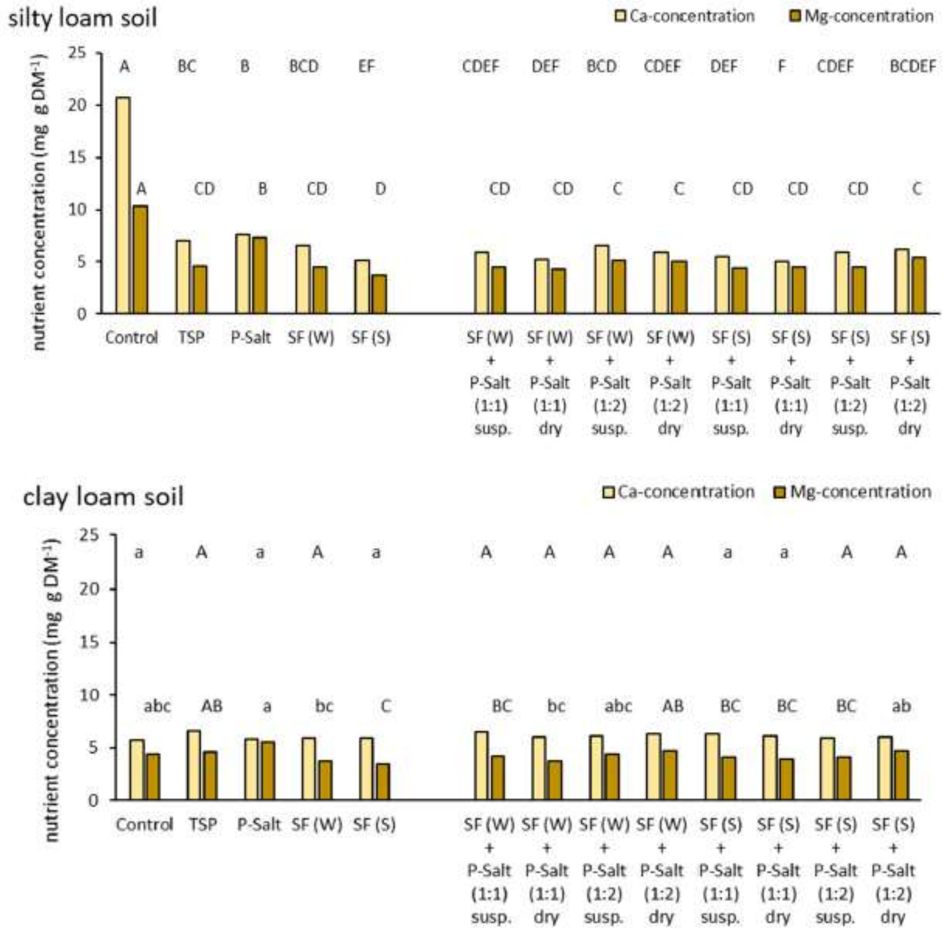

Figure 4. Maize P-, Ca- and Mg concentrations [mg g DM^{-1}] after soil treatment with different recycled digestate fertilizers in a total dose equivalent to 150 mg P (kg $soil^{-1}$). Please see Figure 3 for all other details. Data are means of four replicates each. Different letters denote significant differences (two-factorial Tukey's test with $p \leq 0.05$). Lowercase and uppercase letters indicate significantly different mean values between both soil types. Uppercase letters for both soil types indicate no significant difference.

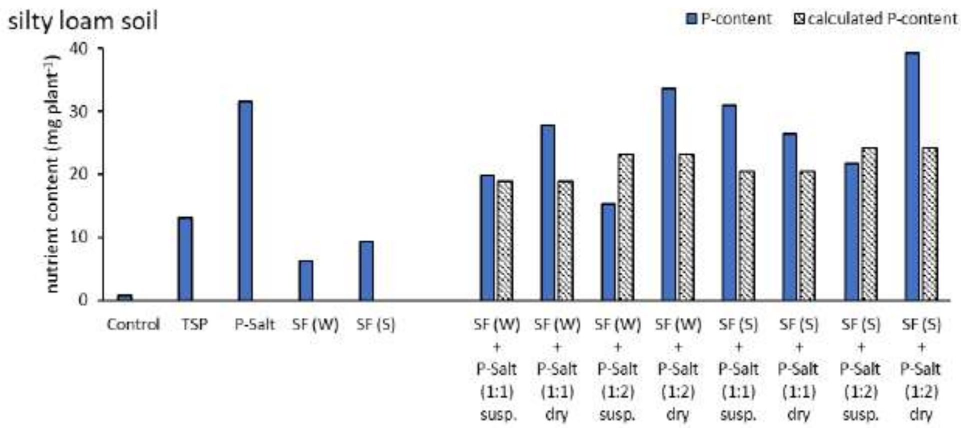

Figure 5. *Cont.*

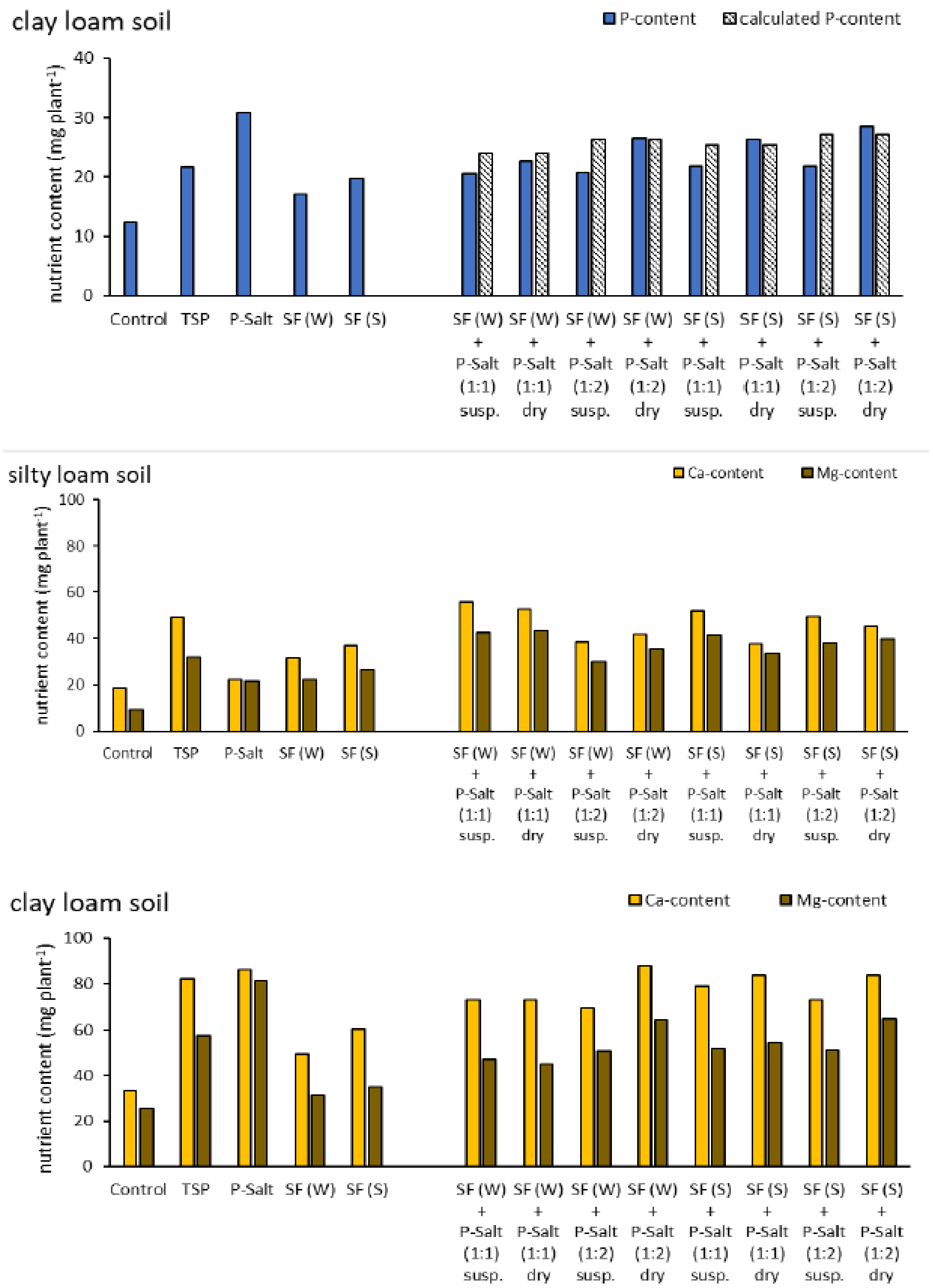

Figure 5. Total and calculated content per plant of P (P-content, calculated P content), and total content of Ca and Mg (Ca/Mg-content) in maize in mg/plant after soil treatment with different recycled digestate fertilizers in a total dose equivalent to 150 mg P (kg soil^{-1}). Please see Figure 3 for all other details. "Calculated P-content" represents a mathematical calculation of the combinations based on the results of the measured P-concentration of each single component (P-Salt, SF(W), SF(S)) to indicate possible additive effects (see material and methods: evaluation of synergistic effects, Equations (1) and (2)). Data are means of four replicates each.

Like in the silty loam, a single application of P-Salt resulted in the highest P-content per plant grown in the clay loam, and treatments with SF (W) or SF (S) alone were less effective but still at the level of TSP. Differences between the combination treatments were generally less pronounced and absolute P net uptake was mostly equal or higher compared to TSP, with a slight advantage of dry vs. suspended soil treatment. All combination treatments (SF + P-Salt), except for SF(S) + P-Salt (1:1) and (1:2) dry, resulted in similar or much lower P-contents than theoretically calculated from the single components' P-content, indicating no synergistic effect between both fractions. Ca-content was increased for all fertilizer treatments, with highest content with TSP, P-Salt and SF(W) + P-Salt (1:2) dry application. The other fertilizer combinations also resulted in increased Ca-contents compared to the single solids (SF(W/S). Advantages of the combination treatments were observed with dry application technique, whereas different ratios had no effect. The single solid treatments resulted in increasing Ca-content for SF(S) compared to SF(W) treatment, with lowest Ca-contents with SF(W) compared to all other fertilizer treatments. Mg-content was the highest with P-Salt fertilizer followed both combination treatments SF(W/S) with higher P-Salt ratio (1:2) and dry application. Slightly increased Mg-contents were observed for SF(S) combination treatments compared to SF(W). Single solids (SF(W/S) resulted in lowest Mg-contents, slightly higher for SF(S) compared to SF(W) and both significantly higher compared to the control.

3.3. Effect of P-Fertilizers on Plant Available P (CAL-P) in Soil

The CAL-P concentration in the soil solution, defined as the fraction being available to plants, was determined in parallel to the P-concentration in the plants in order to record the P-availability in the root zone as a function of the different fertilizer scenarios. Results are shown in Table 3.

Table 3. CAL-extractable P (CAL-P) in soil.

P-Sources	Application Technique	CAL-P 2 Days after Fertilizer Incubation	CAL-P after Maize Harvest	CAL-P 2 Days after Fertilizer Incubation	CAL-P after Maize Harvest
		Silty Loam [mg kg^{-1}]	Silty Loam [mg kg^{-1}]	Clay Loam [mg kg^{-1}]	Clay Loam [mg kg^{-1}]
Control		24 G	15 F	73 g	54 e
TSP		61 F	142 AB	121 cde	97 cd
P-Salt		205 A	173 A	151 abc	139 a
SF(W)		97 E	52 E	78 fg	91 d
SF(S)		68 F	59 E	94 efg	101 bcd
SF(W)+P-Salt (1:1)	suspended	113 CDE	80 D	123 BCDE	115 abcd
	dry	130 BCD	123 BC	103 def	109 ABCD
SF(W)+P-Salt (1:2)	suspended	101 DE	125 BC	117 CDE	110 ABCD
	dry	147 BC	138 ABC	141 ABC	133 AB
SF(S)+P-Salt (1:1)	suspended	104 DE	104 CD	161 ab	105 ABCD
	dry	145 BC	129 ABC	146 ABC	122 ABCD
SF(S)+P-Salt (1:2)	suspended	151 B	119 BC	167 A	127 ABC
	dry	148 BC	139 ABC	135 ABCD	110 abcd

CAL-extractable P (CAL-P) in mg kg^{-1} soil cultivated with maize after soil treatment with different recycled digestate fractions in a total dose equivalent to 150 mg P (kg soil^{-1}); fractions were P-Salt (P-enriched precipitate from the liquid fraction), SF (W) (air-dried solid fraction), SF(S) (steam-dried solid fraction), and different combinations of them compared to unfertilized control and triple superphosphate (TSP); CAL-P was measured 2 days after fertilizer incubation prior to seeding and after maize harvest; please see Figure 1 for all other details. Data are means of four replicates each. Different letters denote significant differences (two-factorial Tukey's test with $p \leq 0.05$). Lowercase and uppercase letters indicate significantly different mean values between both different soil types. Uppercase letters for both soil type treatments indicate no significant difference.

All tested P-fertilizers significantly increased the free CAL-P concentration in the silty loam compared to the untreated control. This was observed directly after fertilization and after harvest of the maize plants. The CAL-P after fertilization (measured 2 days after dosing) was lowest in the untreated control (24 mg/kg soil) and highest in the soil fertilized with P-Salt (205 mg/kg soil). Compared to this, the reference TSP and the solid SF(S) had relatively low initial CAL-P concentrations with levels similar to the control. SF(W) resulted in slightly higher CAL-P compared to SF(S). The combination treatments resulted in higher CAL-P than the single solids alone, but lower than the P-Salt alone. The CAL-P was slightly increased with dry application technique, except for SF(S) + P-Salt (1:2). However, after harvest, the CAL-P in soil with TSP treatment had more than doubled. SF(W) and SF(S) fertilization showed, in contrast, higher initial P-concentrations that slightly decreased at harvest. By far, the highest initial and also terminal CAL-P-concentrations in soil were found after treatment with P-Salt alone. Combinations of fertilizer fractions lead to highest CAL-P-concentrations when P-Salt was applied dry in a ratio of 2:1 or 1:1, both leading to a level lower than P-Salt alone and the reference TSP. Significant differences in the application techniques (suspended or dry) were only noticed for SF(W) + P-Salt (1:2) and SF(S) + P-Salt (1:1) with higher CAL-P concentrations with the dry application technique. However, at harvest, the CAL-P concentrations in the soil had generally decreased, except with TSP which increased the final concentration a lot (up to 173 mg/kg soil). Interestingly, the combinations of P-Salt and SF resulted in a relatively constant available P level at harvest around or higher than 100 mg/kg soil. Significant differences in the application techniques (suspended or dry) were only noticed for SF(W) + P-Salt (1:1) again with higher CAL-P concentrations with the dry application technique.

In the clay loam, the tested P fertilizers showed higher P concentrations in the soil compared to untreated controls right after fertilization, except for (SF(W/S) that resulted in similar concentrations as the control of ca. 73/78/94 mg/kg soil. Highest CAL-P could be measured for P-Salt and the combination treatments SF(W) + P-Salt (1:2) dry, SF(S) + P-Salt for both ratios (1:1 and 1:2) and the suspended and dry application technique, especially after harvest for P-Salt alone. The solid SF(W) had low CAL-P after fertilization similar to the control, but after harvest CAL-P concentration was a bit increased to the level of TSP. Differences between SF(W) and SF(S) could be noticed after fertilization and after harvest with increased CAL-P with SF(S). Only slight CAL-P differences for the combinations of SF(W) + P-Salt after fertilization and after harvest were detected with increased CAL-P for the 1:2 ratio together with dry application. The combination with SF(S) + P-Salt resulted in higher CAL-P compared to the combinations with SF(W). The different application technique showed no significant effects.

4. Discussion

4.1. Effects of P-Fertilizers on Biomass Yield, Plant Nutrient Uptake, and CAL-P in Soil

P-enriched salt (P-Salt), recovered from the liquid fraction of a biogas plant digestate by alkaline precipitation, increased the dry matter (DM) yield of maize shoots, grown in a clay loam agricultural surface soil for 50 days. The increase was significant compared to a mineral reference fertilizer (TSP), dosed to the soil in P-equivalent, single pre-emergence amounts of 150 mg/kg. With respect to the absolute amount of P given in comparison with the minimum P content requirements defined by the German Fertilizer Ordinance [37] for different fertilizers (w/w content of P in Thomas phosphate 4.4%, superphosphate 7.0%, dicalcium-phosphate with Mg 8.7%), the precipitated P-Salt used in this study with a P content of 11% (w/w) was within that range [38]. The application of both fertilizers resulted in similar P concentrations in maize shoot dry matter. The absolute total P content after treatment with P-Salt was even higher than with TSP. Similar results were reported by Ehmann and Bach [39] in ornamental plants, and by Ehmann et al. [40] on spring barley and *Vicia faba* L. beans in different soils using P-Salt from pig manure recovered by the same P recycling process as in our study. Further studies from Vogel et al. [41], Lekfeldt et al. [42], Vaneeckhaute et al. [43], Cabeza et al. [1], Römer and Steingrobe [44], who had used other recycled, P-enriched fertilizers from different sources, also showed that these products have high potential as P fertilizer. These findings indicate that P-enriched materials, derived from biological waste, can be effective P fertilizers that may reduce the use of mineral P sources. Likewise, struvite (ammonium magnesium phosphate) as a prominent example of recycled P from wastewater and sludge [45] was reported to perform as an effective slow release fertilizer [46].

The practical use as fertilizer, however, is highly dependent on the plant availability of the P components in the soil. P mobilization and uptake by soil microbes and plant roots play a vital role for crop yield [47]. In the presence of recycled P components, critical soil components may still be lacking in nutrient-poor soils, as can be seen in the results from the nutrient–depleted silty loam subsoil used in this study, where the effect of P-Salt on DM yield was lower than the reference TSP. An addition of the recycled solids (SF(W), SF(S)), however, resulted in similar DM yield compared to TSP. Obviously, the P-fertilization success depends on the soil/rhizosphere-plant continuum, as also mentioned, e.g., by Hinsinger [48] and Shen [8]. These authors reported that plants can make use of P fertilizers with low plant availability by changing the conditions in the rhizosphere e.g., through the change of pH or the release of phosphatases. An important mechanism of P release has also been attributed to mycorrhiza communities in the rhizosphere. The relationship between nutrient supply and enzyme activity is regulated by a negative (reciprocal) feedback mechanism [49]: when the nutrient supply is low, the enzyme activity is induced, and vice versa. The above may be an explanation why the addition of recycled digestate solids positively influenced the rhizosphere of the nutrient poor soil with respect to P mobilization and uptake by the plant. Possible mechanisms for this conditioning effect, defined as any ability to enhance crop yields and/or improve soil performance for any soil function, could be of physical (soil structure, gas exchange, water availability) or/and microbiological (soil microbiome, plant–microbe interactions) nature [50].

Triple superphosphate (TSP) is a mixture of calcium dihydrogen phosphate and monocalcium phosphate, $[Ca(H_2PO_4)_2 \times H_2O]$. A high proportion of P in TSP is directly water soluble, so that P is immediately available for plant uptake [1]. In contrast, the water solubility of P in P-Salt is very low. $NaHCO_3$ and H_2SO_4 can increase P solubility to 30–50% (Table 1). The exact mechanism of P mobilization from P-Salt is yet unknown. However, it is likely that processes in the rhizosphere, also facilitated by the dried solids of the digestate, are responsible for P mobilization. The slow but continuous release of P from P-Salt regulated in the rhizosphere may therefore represent a depot effect of this material in comparison to TSP, which, due to its high water solubility, might be subject to rapid immobilization in soil, making it rapidly unavailable to plant roots. The different results in the two soils tested in this experiment indicate that the recycled solids (SF(W), SF(S)) may act to enhance P-Salt utilization in soils that have low P content and insufficient P mobilization capability. Support for the hypothesis that the rhizosphere regulates P comes from our CAL-P measurements in the tested soils two days after fertilization and at harvest. Despite the differences in solubility, the measured CAL-P concentration after single P-Salt dosage and in all combinations with SF were equal or higher compared to TSP in both soils (both initially and after harvest).

A high correlation between plant DM yield and CAL-P in the agricultural clay loam soil was observed (Figure 3 vs. Table 3). Lowest DM and CAL-P were found in untreated controls, highest values after treatment with P-Salt. SF(S) alone was superior to SF(W) in both parameters. All combinations were comparable with TSP and only showed almost insignificant variability between each other. In the silty loam subsoil, correlation of both parameters was also given between the recycled solids (SF(S) > SF(W)). Like in the clay loam soil, differences between the combinations were generally low. The low effect on DM yield for P-Salt alone, however, was not correlated with low CAL-P in this soil. Here, DM yield was rather negatively correlated with the CAL-P. Likewise, in the mixtures, the negative effect of higher proportions of P-Salt on DM yield was rather inversely correlated with the CAL-P results. However, when compared to P concentrations in plant, the high

CAL-P for P-Salt alone and partly for the 1:2 combinations correlated well with the highest P-concentrations. Possible explanations for these two effects are: (1) that P-Salt contains a fraction that is easily water-soluble and available for immediate plant uptake and (2) that high P content in the plant may have an inhibitory effect on plant DM.

Support for hypothesis (1) comes from the finding that the measured concentrations of Mg and Ca in P-Salt fertilizer were high (Table 1), making it likely that a minor but significant portion of P in the P-Salt fraction is partly bound in Ca and Mg-Salts that are readily available in soil and easily taken up by plants [51,52], similar to TSP. Indeed, when comparing the Ca and Mg content in the maize shoots with DM yield, high Ca and Mg content in the plants mostly correlated with high DM yield in both soils. The fact, that the Mg and Ca status of maize plants is a reliable indicator for plant growth and yield was reported, e.g., by Potarzycki [53], Lecourieux et al. [54] and Szczepaniak et al. [55].

In summary, the results of this study show that P-Salt alone and combinations with solids recovered from a biogas digestate can be an effective fertilizer alternative to TSP in an agricultural surface soil typical for maize growth. Single doses of P-Salt at equimolar P-levels resulted in equivalent or higher values for three indicators of yield and nutrient supply, namely plant DM, P content and soil CAL-P concentration. In the silty loam subsoil, a model for a P depleted soil with low microbial activity, the P fertilization effects of P-Salt alone were also comparable to TSP regarding P content and soil CAL-P. In this situation, however, a mixture of P-Salt with the co-isolated solid fraction (SF) of the digestate was necessary for a plant DM yield comparable to TSP. A systematic analysis of synergistic effects between both recycled fractions is discussed below.

4.2. Fertilizer Effects of Different Fertilizer Combinations and Soil Application Techniques

Synergistic effects on DM yield were observed for combinations of P-Salt with different solid fractions of recycled biogas digestate (SF(W), SF(S)) mostly in the nutrient poor silty loam subsoil and less in the agricultural surface soil. This leads to the conclusion that the isolated solids might have a soil conditioning effect, especially on soils with low nutrient content by adding or stimulating soil microbial activity.

In a parallel study reported by Ehmann and Bach [39], recycled fertilizers produced identically to this study in the same biogas plant, were tested with sunflowers in a horticultural growth substrate in a greenhouse pot experiment. Synergistic effects of P-Salt and air-dried solids (SF(W)) on DM yield were also observed. Similar results were reported by Ehmann et al. [40] in greenhouse pot experiments. Other authors reported soil conditioning effects of recycled organic waste and biochars that enhanced the effect of organic fertilizers, improved soil quality [40,50,56] and decreased the need of inorganic fertilizers [57–60].

Regarding the combination of SF to P-Salt, a 1:1 ratio was almost as efficient as a ratio of 1:2 in the silty loam subsoil for DM yield, P concentration in plants and CAL-P. For the clay loam soil only slightly increased DM matter yields were observed for 1:2 ratios compared to 1:1, especially with dry application. Given that the concentration of P in the solids was considerably lower than in P-Salt, the results with combined fertilizers in the clay loam surface soil indicate the potential of the solid fractions to reduce the total amount of P-Salt needed, to be equally efficient as TSP. For practical use, the ratio between the recycled fertilizer components may therefore need to be optimized individually to the agricultural situation.

A comparison of the different application techniques revealed a slight advantage of dry vs. suspended application for DM yield increase and total P content in the plants. The low difference between both application techniques demonstrates that the process of adding the different fertilizer components to the soil is relatively robust for practical use. Suspension of the components may be more suitable in greenhouse horticulture, whereas dry application of solids would be more applicable on arable land.

4.3. Effects of Different Drying Procedures of the Solids (Air Dried vs. Steam Dried) on Fertilization

The treatment with the two different dried solid fractions - air-dried at 40 °C (SF(W)) and steam-dried at 120 °C (SF(S))—resulted in significant differences in DM yield, concentration and content of P, Mg and Ca in maize plants in both tested soils. Increased DM yield and nutrient content of P, Ca and Mg were observed with SF(S) treatment compared to SF(W) in both tested soils, whereas differences in CAL-P were less pronounced.

The chemical characterization of the recycled solids is shown in Table 1. In addition to an alkaline pH (8.5), SF(S) had only half the concentration of H_2SO_4—soluble P (sparingly plant available). SF(W) on the other hand, was shown to remain virtually unchanged during drying as shown by Awiszus et al. [25].

Different authors have reported that high-temperature drying processes of organic waste/material decrease the amount of organic P and increase the fraction of inorganic (more bio-available) P, a form of phosphorous that can be directly absorbed by plants (e.g., [61–64]). Despite the expectation that higher drying temperatures (here 120 °C for SF(S)) might negatively influence biological indicators of the fraction, a negative effect on plant growth could not be observed. One of the reasons might be the relatively high heat resistance of soil phosphatases, as reported by Eivazi et al. [65].

The process of superheated steam drying is well known in the foodstuff industry [66]. Superheated steam transfers its heat gently to the product to be dried and the water to be evaporated and, thus, acts both as heat source and as drying medium. The process results in much lower particle size and increased homogeneity of the material. This may contribute to the positive effects observed for SF(S) compared to SF(W).

5. Conclusions

The utilization of P recycled products as fertilizer is an important strategy to close nutrient cycles in agriculture and to save nutrient resources. The presented data demonstrate an obvious benefit of the use of P recycled fertilizers from a biogas digestate on agricultural soils. Our results show that effects were comparable to or even stronger than conventional triple superphosphate (TSP). Indicators for fertilizer efficacy in this study were (a) plant dry matter (DM) yield, (b) plant P concentration and content, (c) plant Ca and Mg concentration and content and (d) CAL-P in soil.

The ratio between the isolated fractions ("P-Salt", "solids") was decisive for the magnitude of effects on plant (DM), P concentration and absolute content in plants and P concentration in soil (CAL-P). In a nutrient-poor soil, synergistic effects between the fractions were observed, most likely due to an induced increase of the originally low microbial activity in the soil. Steam drying of the recycled solid fractions resulted in higher fertilizing effects compared to air-drying. Results of this greenhouse experiment indicate that recycled P-Salt and combinations with solids can be used as sustainable substitute for mineral P fertilizers.

The specific conditions in this study, namely soil, crop, and environmental conditions, may not be applicable to other specific agronomical situations. Furthermore, a more detailed analysis of the chemical composition of the recycled fertilizers would be helpful to understand effects and possible unwanted side effects of the material used. Dry matter as an indicator for crop yield is useful for energy crops like maize but may not reflect the yield situation for other crops at harvest.

Further research is needed to understand underlying processes and effects. Other combinations and ratios of the single products might cause different effects in different soils depending on biological processes through P mobilization and soil pH effects. Moreover, the P fertilizers were investigated in pot experiments only, and further confirmation is needed in field experiments over longer time scales (soil P processes are much slower compared to N processes) and for a wider range of soil types and cropping systems. Results would lead to a better agronomic management of recycled products as P fertilizers involving soil and rhizosphere processes and improving P-recycling efficiency in the future.

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5 Efficiency of Phosphorus Fertilizers Derived from Recycled Biogas Digestate as Applied to Maize and Ryegrass in Soils with Different pH

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Abstract: Three phosphorus (P) fertilizer fractions recycled from biogas digestates were tested alone and in combination for their efficiency in two agricultural surface soils with different pH: a silty sandy loam and a clay loam. The experiments were carried out in pots under greenhouse conditions, using mineral triple superphosphate (TSP) as a reference. Maize was cultivated for 50 days, followed by ryegrass cultivation for an additional 84 days in the same soil, without additional fertilization. The variables investigated were above-ground plant biomass production, plant phosphorus concentration and content, and plant available phosphorus concentration in soil. The dry matter (DM) yield of maize was increased by the organic P fertilizers equal to or more than TSP in both soils. In the neutral soil, biomass was almost doubled compared to TSP when using one of the fractions (Struvite containing P-Salt) alone or in combination with dried solid fractions. P concentration in maize cultivated in the neutral soil was not significantly different between the P fertilization treatments. However, associated with biomass increase, the total P content in maize plants was equal to or higher than that with TSP. In the acidic soil, P concentration and total P content in maize plants, as well as the calcium-acetate-lactate extractable P (CAL-P) concentration in soil, were equal to or even higher than TSP. Ryegrass DM yield was unaffected by all P fertilizers, independent of the soil, although P concentration and total P content increased in the acidic soil with all fertilizers. Our results show that recycled P fertilizers from biogas digestates are effective P fertilizer alternatives to mineral TSP for maize cultivation under acidic and neutral soil conditions. The lack of growth effects in ryegrass indicates that recycled P fertilizers do not require changes in weed control. On the other hand, P extraction by ryegrass in overfertilized acidic soils as an option for soil remediation also works in soils fertilized with biogas digestate fractions.

Keywords: recycled phosphorus fertilizer; biogas digestates; soil pH; phosphorus fertility indicators; maize; ryegrass

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1. Introduction

Phosphorus (P) is an essential nutritional element for plant growth and development, and sufficient P supply is a key factor for plant quality and yield in agricultural production [1]. Only a small fraction of the soil P is available to plant roots in the soil pore water fraction, because P is quickly adsorbed and immobilized onto soil particle surfaces [2–4]. The intensive use of organic and inorganic fertilizers in agriculture in recent decades has resulted in high P accumulation in soils [5] that is unavailable to plants [6]. In Europe, agricultural soils are estimated to contain 100–3000 mg P/kg, corresponding to 130–3900 kg/ha in the top 10 cm of the soil [3]. Worldwide, approximately 88% of agricultural P fertilizer comes from the limited resource phosphate rock [7], available only at a few locations worldwide in quantities that may secure supply for the next few hundred years (calculated from [8]). Many countries in the world, including the European member states, depend on imports from these regions and are thus susceptible to world market price fluctuations and economic and political crises [9,10]. Accordingly, the European Union has listed mineral phosphate rock (2014) and phosphorus (2017) as critical raw materials [11,12]. As a result, the activities to make more efficient use of renewable secondary phosphate resources [13,14], with similar characteristics as compared to standard mineral fertilizers, have increased in the last years.

A variety of P sources and recycling technologies have been investigated, and struvite ($MgNH_4PO_4 * 6H_2O$), recycled from, e.g., sewage sludge, was identified as a slow-release fertilizer that offers a sustainable alternative to conventional phosphate rock-based fertilizers [15]. With the increase of biogas production in European countries from 6227 plants in 2009 to more than 17,000 plants 2017 [16], biogas digestates have become increasingly available as a P source, particularly in areas with high livestock densities. Compared to this, the P fertilizer consumption increased to 248,000 tons [17] in 2019/2020. At least parts of the German P consumption could be covered by digestates. They contain high amounts of P [18] and thus have a potential as valuable fertilizers or soil amendments [19]. Enrichment of P in fertilizers produced from biogas digestates has been identified as a key technology to produce storable and transportable P fertilizers [20]. One of the major challenges for P recycling from organic material is the formulation of products with high plant availability in the soil root zone. Plant uptake can considerably differ [21] across recovered products, depending on the proportion of organic P in the enriched fractions. Plants may invest substantial photosynthetic energy to access soil P through active P mobilization from less soluble fractions [22]. Promising concepts to increase P uptake and use efficiency are thus the use of highly P-efficient crop genotypes with a potential for high soil P mobilization in combination with P placement in the root zone, P-mobilizing bioeffectors and potentially P-mobilizing legumes in crop rotation [3].

Within the research project GOBi (General Optimization of Biogas Processes, grant agreement No. 03EK3525A) funded by the German Federal Ministry of Education and Research (BMBF), a technology for the recycling of P from biogas digestates and potentially also from liquid manure (slurry) was developed. The process resulted in three different P-enriched, storable and transportable fertilizer fractions, named P-Salt, warm-air dried solid (SF(W)) and steam-dried solid (SF(S)). Struvite is a substantial part of the P-Salt. First results regarding the efficiency of these fractions in maize and ornamentals were described by [23,24].

An important factor influencing P availability to plants is the soil pH. Ref. [25] addresses several reports in their publication, which found a correlation between low pH and increased solubility of P in soil, and a decrease in P sorption and increase of P uptake into plants [26–30]. Some recycled P fertilizers from different sources have been tested with various soils, showing significant differences in P availability, depending on the recycling process, the soil type and the soil pH [23,24,31–33]. Therefore, the objective of this study was to assess the influence on the fertilizer P efficiency of the three recycled P fractions and its combination treatments at different pH levels.

In the present study, the efficiency of P fertilizers, recycled from digestates of a biogas plant with the technology of the GOBi project, was tested using two agricultural soils with an acidic and a neutral pH. The experiments were conducted in a greenhouse pot setup, with maize as the primary crop and ryegrass as the subsequent culture, using TSP as reference fertilizer. In addition to the direct comparison of the fertilizer fractions, the combined application of dried solid fractions and P-Salt has previously shown synergistic effects on P efficiency [23]. Therefore, combinations were tested under identical experimental conditions to assess differences in the P fertilizer efficiency from recovered and commercial fertilizers in soils that differ in pH, texture and nutrient content. Maize was used in this study because it is one of the most widespread and versatile agricultural crops worldwide, used for different elements in human nutrition, animal feed and bio-energy production [3].

The *Zea mays* L. var. 'Carolinio' used here is a specific variety for use as a biogas substrate, with a high dry matter yield potential. Perennial ryegrass is, on the one hand, the most used grass species for sowing grasslands in temperate areas, and on the other hand, it is also a widespread weed in European agricultural soils. A second objective was the evaluation of the influence of recycled fertilizers on the growth and P uptake potential of ryegrass compared to TSP.

Based on the experimental results with the same recycled material as described above, the following hypotheses were established and tested in this study:

- Compared to a mineral P fertilizer (TSP), fractions recycled from biogas digestates can be effective P fertilizers over a range of soils differing in pH conditions (5.5 and 7.4), with advantages in acidic soils.
- Combined treatments (P-Salt + SF W/S) result in a higher P bioavailability, with synergistic effects, compared to the single application in both soils.
- Ryegrass as a widespread weed does not benefit from recycled P fertilizers with regard to biomass production, and thus, its use does not require changes in weed control.
- Ryegrass cultivation as an option for soil remediation after use of excess mineral P can also be used after application of recycled P fertilizers.

2. Materials and Methods

A greenhouse experiment with maize was conducted in two different soils using three recycled P fertilizers produced from biogas plant digestates. Fertilizers were tested alone or in paired combinations, in comparison to a mineral fertilizer (Triple superphosphate, TSP) and an unfertilized control. After maize harvest, ryegrass was sown and cultivated in the same soil for another 84 days, without additional P fertilization. Variables evaluated were above-ground plant biomass, biomass P concentration and total P content in plants, and soil CAL-P.

2.1. Recycled P Fertilizers

Three P fertilizers were derived from the liquid and the solid part of the biogas digestate from a pilot plant (Fraunhofer IGB, Kupferzell, Germany) operating with a mixture of cow manure and maize silage. The process overview is described by [34]. The first fraction was a P-enriched precipitate ("P-Salt") recovered by alkaline precipitation from the liquid fraction of the digestate after several process steps. The final dried and milled product was a mixture of struvite, calcium phosphate and magnesium phosphates. Two types of solids were recovered from the solid fraction of the digestate, either dried at 40 °C as air-dried separated solids, "SF(W)", or dried with a steam-dryer at 120 °C as steam-dried separated solids, "SF(S)". The measured total P content (Pt) of P-Salt was 11.3% DM, SF(W) contained 2.1 Pt in % DM and SF(S) 2.3 Pt in % DM. Details about the separation and recycling process, the measured P contents and other nutrient concentrations of the three fertilizer fractions are given in Table 1 of [23].

All P fertilizers and their combinations were applied at the standard supply rate for maize of 150 mg total P per kg soil (lab standard dose for P supply) once at the beginning of the experiment. P concentrations measured in the used fertilizer fractions were taken as reference to calculate the corresponding dose weights of single doses or combinations. Two combinations were tested, where P-Salt was combined with SF(W) or SF(S) in the ratio 1:1. For combined fertilizers, the absolute amounts of each fraction were calculated and used accordingly to match the desired total dose of 150 mg total P per kg soil. A ratio of 1:1 represented 75 mg total P per kg soil from the P-Salt and 75 mg total P per kg soil from the separated solid fraction to add up to a total amount of 150 mg total P per kg soil. Application was done by homogeneously mixing both components into the soil sequentially (first P-Salt, followed by SF(S/W)), which corresponded to the "Dry" application in [23].

2.2. Soil Characteristics

The experiments were carried out using two agricultural surface soils, selected for their low CAL-P and different pH ($CaCl_2$). The CAL-P, defined as P extractable in calcium-acetate-lactate solution, was determined according to [35]. The silty sandy loam with pH 5.5 was collected from a low-fertility grassland in Speyer, Germany. The clay loam with pH 7.4 was collected from an agricultural field in Kleinansbach, Germany.

2.3. Soil Sampling and Analysis of P, K, Mg and pH

Soil samples for soil characterization were taken prior to the initial P fertilization and after ryegrass harvest (84 days after maize harvest, 134 days after P fertilization). All samples were stored at −20 °C until analysis. Plant available P in soil (dried at 105 °C and sieved to 2 mm) was determined using the CAL extraction method [35], followed by flame photometric quantification. The same method was used for K and Mg determination. Soil pH was measured in a suspension with 0.01 M $CaCl_2$ [36].

2.4. Experimental Details

The first part of the experimental setup used in this study was identical to the pot experiment with maize described in detail by [23]. The three recycled P fertilizers and the combinations were applied in comparison to the reference fertilizer TSP and an unfertilized control. An overview of the experimental setup is given in Table 1 and Figure 1.

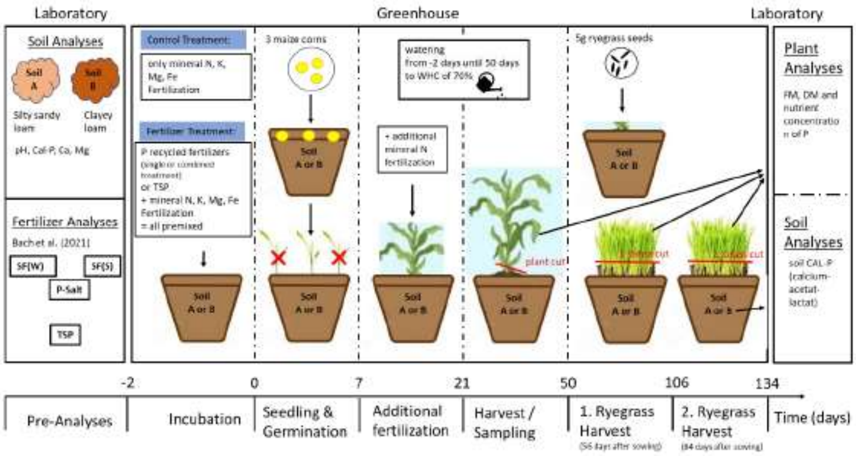

Figure 1. Experimental setup of the greenhouse pot experiment with maize followed by ryegrass. Fertilizer fractions tested were P-Salt, SF(W); SF(S), and two combinations of them, compared to unfertilized control and triple superphosphate (TSP). Maize plants were cultivated for 50 days in a silty sandy loam and clay loam soil. After maize harvest, ryegrass seeds were cultivated for 84 days with two ryegrass cuttings 56 and 84 days after sowing. DM: dry matter; FM: fresh matter; Ca: calcium, Mg: magnesium; K: potassium; N: nitrogen; Fe: iron; WHC: water holding capacity.

Soil (3 kg dry weight per pot) was mixed homogeneously with the dry P fertilizer fractions and filled into round plastic pots (4 L volume, 20 cm diameter). Only the conventional fertilizer TSP was pre-mixed with de-ionized (DI) water to ensure exact dosage of the small amounts. Additional mineral fertilizer (Ammonium nitrate (NH_4NO_3), Potassiumsulfate (K_2SO_4), Magnesiumsulfate ($MgSO_4$), Fe-Sequestren (Ferric EDTA)) was given once to each pot, including the untreated controls. After fertilization, the soil was mixed again, watered to 70% of its maximum water holding capacity (WHC) and incubated for two days in a greenhouse at 24 °C before sowing the maize seeds (energy crop *Zea mays* L. var. Carolinio (KWS SAAT SE & Co. KGaA, Einbeck, Germany)). Three seeds per pot were sown into each pot at 4 cm depth. After germination, the number of seedlings per pot was reduced to one. A second additional mineral fertilization, only with aqueous Ammonium nitrate, was applied three weeks after germination.

Maize plants were harvested 50 days after seeding, and the remaining pots were then cultivated with perennial ryegrass (*Lolium perenne* L., cv. Arvicola, Feldsaaten Freudenberger GmbH & Co., Germany) for 12 weeks. For this purpose, 5 g of ryegrass seed was incorporated into the top 1–2 mm of the soil and cultivated without any additional fertilization. Identical to the preceding maize cultivation, each pot was irrigated with deionized (DI) water and weight-controlled every three days to maintain a soil humidity of 70% WHC.

Table 1. Experimental setup of the greenhouse pot experiment with maize and ryegrass.

Start Crop	Maize (*Zea mays* L., var. Carolinio) 3 seeds per pot; after germination, reduction to 1 seedling per pot
Soil	Silty sandy loam: Texture sSL; pH ($CaCl_2$) 5.5; nutrient status for P, K, Mg (all CAL) in mg/kg soil: 15, 100, 32 Clay loam: Texture tL; pH ($CaCl_2$) 7.4; nutrient status for P, K, Mg (all CAL) in mg/kg soil): 26, 150, 580
Additional mineral fertilization per pot (excluding P)	200 (mg N (kg soil)$^{-1}$) as NH_4NO_3, 200 (mg K (kg soil)$^{-1}$) as K_2SO_4, 100 (mg Mg (kg soil)$^{-1}$) as $MgSO_4 * 7H_2O$ and 10 (mg Fe (kg soil)$^{-1}$) Fe-Sequestren (6 %). 4 weeks after sowing: 200 (mg N (kg soil)$^{-1}$) as NH_4NO_3
Experimental Duration	Total: 50 days (Time schedule, Figure 1: 0–50 days)
Conditions	Ambient greenhouse conditions (University of Hohenheim, Germany, June 2017); ca. 16 h light, 8 h dark, ca. 20 °C, watering to 70% WHC with DI water (weight control every 2–3 days)
P fertilizer treatments:	
Recycled P fertilizers	All mg below refer to P equivalents per 1 kg dry soil
P-Salt SF(W) SF(S)	150 mg 150 mg 150 mg
SF(W) + P-Salt (1:1) dry	Dry mixed ("dry"): 75 mg SF(W) mixed into the soil, directly followed by + 75 mg P-Salt mixed into the soil
SF(S) + P-Salt (1:1) dry	Dry mixed ("dry"): 75 mg SF(S) mixed into the soil, directly followed by + 75 mg P-Salt mixed into the soil
Control treatments: Triple superphosphate (TSP) Negative control	 Positive Reference; 150 mg DI water
Ryegrass cultivation in the remaining pots (same soils and treatments, same greenhouse conditions):	
Following crop	Perennial ryegrass (*Lolium perenne* L., cv. Arvicola) 5 g seeds per pot
Experimental Duration	84 days from seeding to harvest (Time schedule, Figure 1: 50–134 days)
Harvest (grass cuts)	First cut: 56 days after sowing Second cut: 84 days after sowing
Fertilization	No additional mineral or recycled P fertilization
Irrigation	Watering to 70% WHC with DI water (weight control every 2–3 days)

The pots were set up in a randomized complete block design on tables in the same greenhouse, using four replicates per treatment, resulting in a total number of 56 pots, 28 for each soil type.

2.5. *Maize and Ryegrass Harvest and P Analysis*

Maize shoots were harvested 50 days after sowing. Ryegrass shoots were harvested 56 days and 84 days after sowing. Plant material was collected by cutting the shoots 0.5 cm above the soil surface, followed by determination of dry weight (after drying at 60 °C for 48 h, DM—dry matter). Dried plant material was ground using a laboratory disk mill (TS 250, Siebtechnik GmbH, Mülheim and der Ruhr, Germany) and 0.5 g of the plant material was suspended in concentrated HNO_3 and H_2O_2, followed by microwave extraction at

210 °C for 62 min and filtration. Analysis was carried out by ICP-OES (Agilent 5100, Santa Clara, CA, USA) according to DIN EN ISO 11885 [37]. Shoot P was calculated as concentration (mg/g DM) and as absolute amount per cut (maize: single plant, ryegrass: total cut).

2.6. Evaluation of Synergistic Effects

Possible synergistic effects of P-Salt + SF (SF(W) or SF(S)) were evaluated by calculation of theoretical maize biomass production and maize/ryegrass P content from data with P-Salt and SF applied alone, using the following equation (see also Bach et al.) [23]:

Calculated maize DM yield for ratio 1:1:

$$\text{calculated DM yield} = \frac{\text{SF (W or S) DM yield} + \text{P} - \text{Salt DM yield}}{2}$$

Calculated maize/ryegrass P content for ratio 1:1:

$$\text{calculated P content} = \frac{(\text{SF (W or S) P content} + \text{P} - \text{Salt P content})}{2}$$

Measured values higher than the calculated values after combined application were interpreted as synergistic effect, whereas measured values equal or lower than the calculated ones indicated non-synergistic effects.

2.7. Statistical Analysis

Data analysis was performed using the statistical computing software R version 4.0.4. The effect of the block design, treatments and soil types on different variables (P concentration, DM yield and P content in the plants and CAL-P in soils) was assessed using a two-factorial linear model (n = 4). Data were log-transformed in order to meet the model assumption of normality of residuals and variance homogeneity, when necessary. Least-square means and letter display for pairwise comparison were performed using the R packages emmeans [38] and multcomp [39,40]. Significance was determined at $p \leq 0.05$ using a Tukey test, performed only on finding significant differences in the F-test. Significantly different mean values on different variables were indicated by different letters, and significant differences between the soils were indicated by an asterisk (*).

3. Results

3.1. Effect of P Fertilizers on Maize Biomass Yield and Plant P Concentration

Maize shoot dry matter yield (DM yield) as an indicator for fertilization efficiency is shown in Figure 2. In the acidic silty sandy loam soil (pH 5.5), untreated controls developed the lowest DM yield (7.3 g/plant) compared to all fertilizer treatments. All single treatment groups, including the positive TSP control, were significantly higher in yield, with no significant differences between one another. The highest increase after single dosing was measured with the solid fraction SF(S) (16.45 g DM/plant) and SF(W) (15.08 g DM/plant). The overall highest DM yield (20.48 g/plant) was detected in the (1:1) mixed treatments SF(W)+ P-Salt and SF(S) + P-Salt. Both combination treatments resulted in much higher DM yield than calculated from the single component yields, indicating a synergistic effect between the fractions.

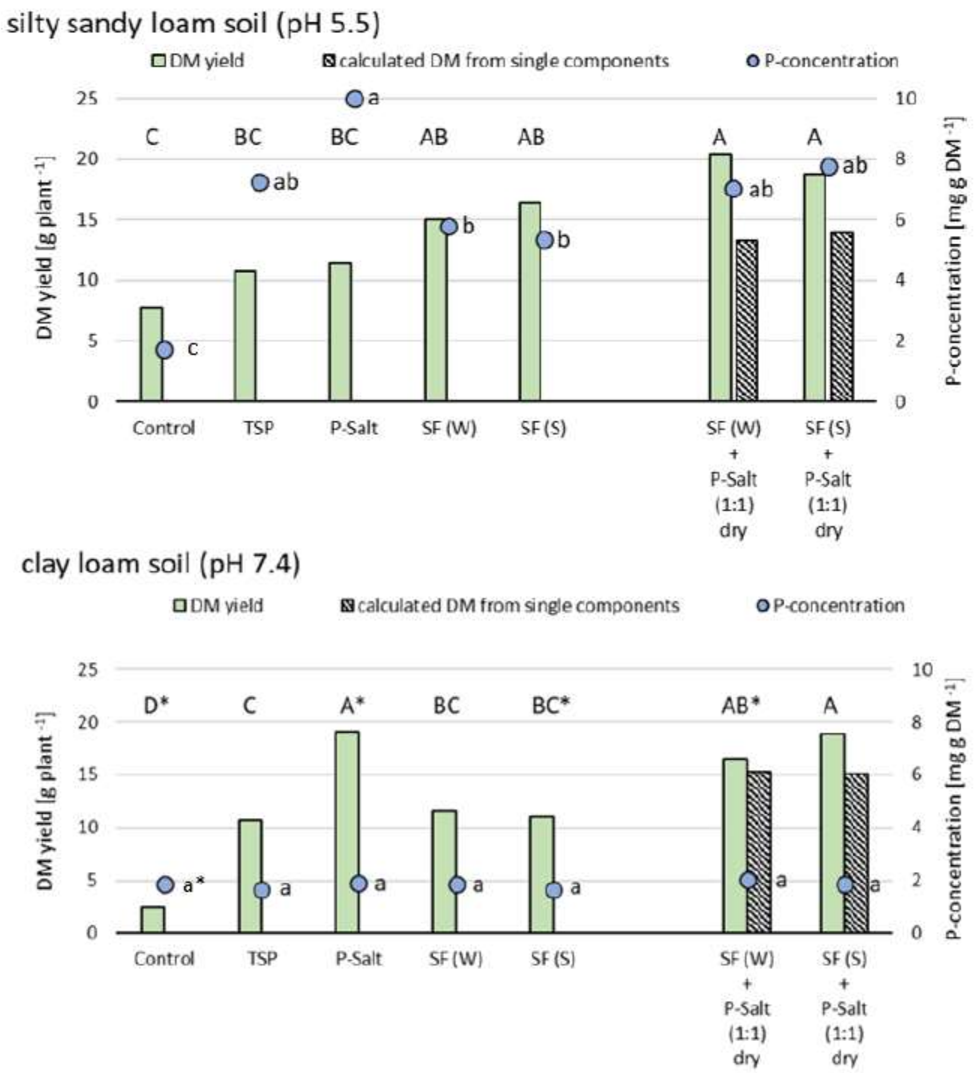

Figure 2. Mean shoot dry matter yield (DM yield) after 50 days in g plant^{-1} and mean shoot P concentration of maize in mg DM plant^{-1} after soil treatment with different recycled fertilizers in a total dose equivalent to 150 mg P (kg soil)$^{-1}$; fractions tested: P-enriched precipitate from the liquid fraction (P-Salt), air-dried solid fraction (SF(W)), steam-dried solid fraction (SF(S)), and two different combinations of them, compared to unfertilized control and triple superphosphate (TSP). Based on the total fertilizer dose corresponding to 150 mg P (kg soil)$^{-1}$, designation (1:1) means that fertilizers were applied with a mass portion of SF (W or S) containing 75 mg P (kg soil)$^{-1}$ + a mass portion of P-Salt containing 75 mg P (kg soil)$^{-1}$. "Calculated DM yields from single components" represent a mathematical calculation of the combinations based on the results of the real DM yield of the single components (P-Salt, SF(W), SF(S)) to indicate possible additive or synergistic effects (see Materials and Methods: Evaluation of Synergistic Effects, equation). Data are means of four replicates each. Different letters denote significant differences (two factorial Tukey test with $p \leq 0.05$), and significant differences between the soils are indicated by an asterisk (*).

Nutrient concentration of P in the maize shoots after harvest as an indicator of nutrient mobilization and uptake into the plants is shown as mg P/g DM yield. Compared to the untreated controls, the P concentration in the maize shoots increased significantly under all fertilizer treatments and especially after treatment with P-Salt alone (10.0 mg/g DM). Compared to the reference TSP (7.26 mg P/g DM), all single and both combined treatments with recycled fertilizer resulted in similar P concentrations in the plants, indicating a sufficient P supply and an efficient P mobilization and uptake in this acidic silty sandy loam soil.

In the neutral clay loam soil (pH 7.4), untreated control plants developed by far the lowest level of DM (2.5 g/plant) compared to all other treatment groups, including those of the acidic soil. Here, P fertilization generally had a much higher relative effect on plant growth compared to the acidic soil. The TSP reference dosing increased DM to 10.7 g/plant, similar to both dried solids, SF(W) and SF(S), in single dosing. In contrast to the acidic silty sandy loam soil, single dosing of P-Salt here had the highest effect of all treatments (19.1 g DM yield/plant), significantly higher than all other single treatments including TSP. Similar to the acidic silty sandy loam soil, differences between the two dried solids were not pronounced, but absolute DM yields with the mixtures were comparable in both soils. A comparison of the calculated yields from single dosing with those of the actually measured yields of both combination treatments indicated slight additive effects of both fraction types.

Despite these high differences in dry matter yield, the P concentrations in plants grown in the neutral soil did not differ significantly between the fertilizer treatments, even including the untreated control. Apparently, the higher pH in this soil limited P availability, and therefore P uptake, to a value not influenced by the different fertilizers.

3.2. *Effect of P Fertilizers on Plant Nutrient Content in Maize*

Since the differences of P concentration between treatments were low, at least in case of the neutral clay loam soil, the data were also evaluated as total P content per maize plant (Figure 3). The objective was to compare the total P in each plant as a result of differences in growth.

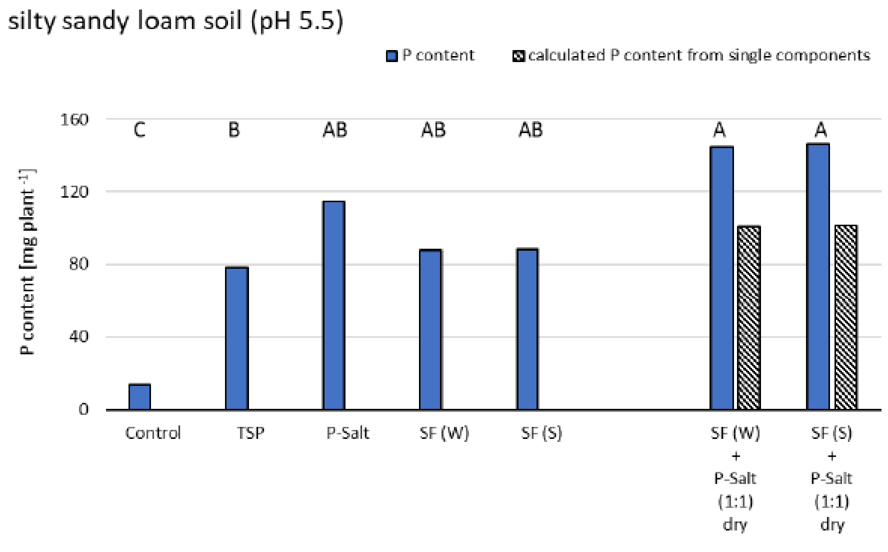

Figure 3. *Cont.*

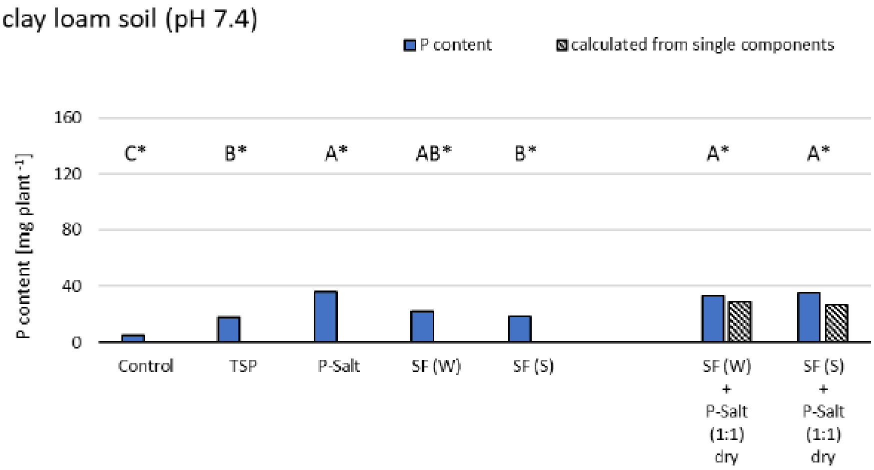

Figure 3. Total phosphorus content (P content) after 50 days in mg plant^{-1} of maize after soil treatment with different recycled fertilizers in a total dose equivalent to 150 mg P (kg soil)$^{-1}$; fractions tested: P-Salt, SF(W), (SF(S), and two different combinations of them compared to unfertilized control and TSP. Based on the total fertilizer dose corresponding to 150 mg P (kg soil)$^{-1}$, designation (1:1) means that fertilizers were applied with a mass portion of SF (W or S) containing 75 mg P (kg soil)$^{-1}$ plus a mass portion of P-Salt containing 75 mg P (kg soil)$^{-1}$. "Calculated P-content from single components" represent a mathematical calculation of the combinations based on the results of the real P contents of the single components (P-Salt, SF(W), SF(S)) to indicate possible additive or synergistic effects (see Material And Methods: Evaluation of Synergistic Effects, equation). Data are means of four replicates each. Different letters denote significant differences (two factorial Tukey test with $p \leq 0.05$), and significant differences between the soils are indicated by an asterisk (*).

In this evaluation, the total P content per plant was increased by all applied P fertilizers in the acidic silty sandy loam. Compared to TSP, the recycled fertilizers had similar or increased effects on P content, with no difference between SF(S) and SF(W). From all single treatments, P-Salt alone resulted in the highest P content. However, when combining the single components SF + P-Salt, both combination treatments resulted in the highest P contents, without differences between each other. A comparison of the calculated P content from single dosing with those of the combinations showed clear differences, indicating once more synergistic effects in this soil.

The P content per plant in the neutral clay loam was generally much lower compared to the acidic soil. Again, single application of P-Salt resulted in the highest P content per plant, and treatments with SF(W) or SF(S) alone were less effective, with a P content similar to TSP. Like in the acidic soil, differences between SF(W) and SF(S) were not significant. Combination treatments were in the order of magnitude of P-Salt alone. Only slight synergistic effects of the combined treatments with SF(W/S) and P-Salt were observed.

3.3. Effect of P Fertilizers on Ryegrass Biomass Yield and Plant P Concentration

Ryegrass dry matter (DM) yield and plant P concentration are shown in Figure 4. DM yield (in g/pot) is shown as stacked bars for the first and the second cut (56 days and 84 days after ryegrass sowing). The P concentration (in mg P/g DM) as an indicator of nutrient availability in the plants is shown as an average across both harvests.

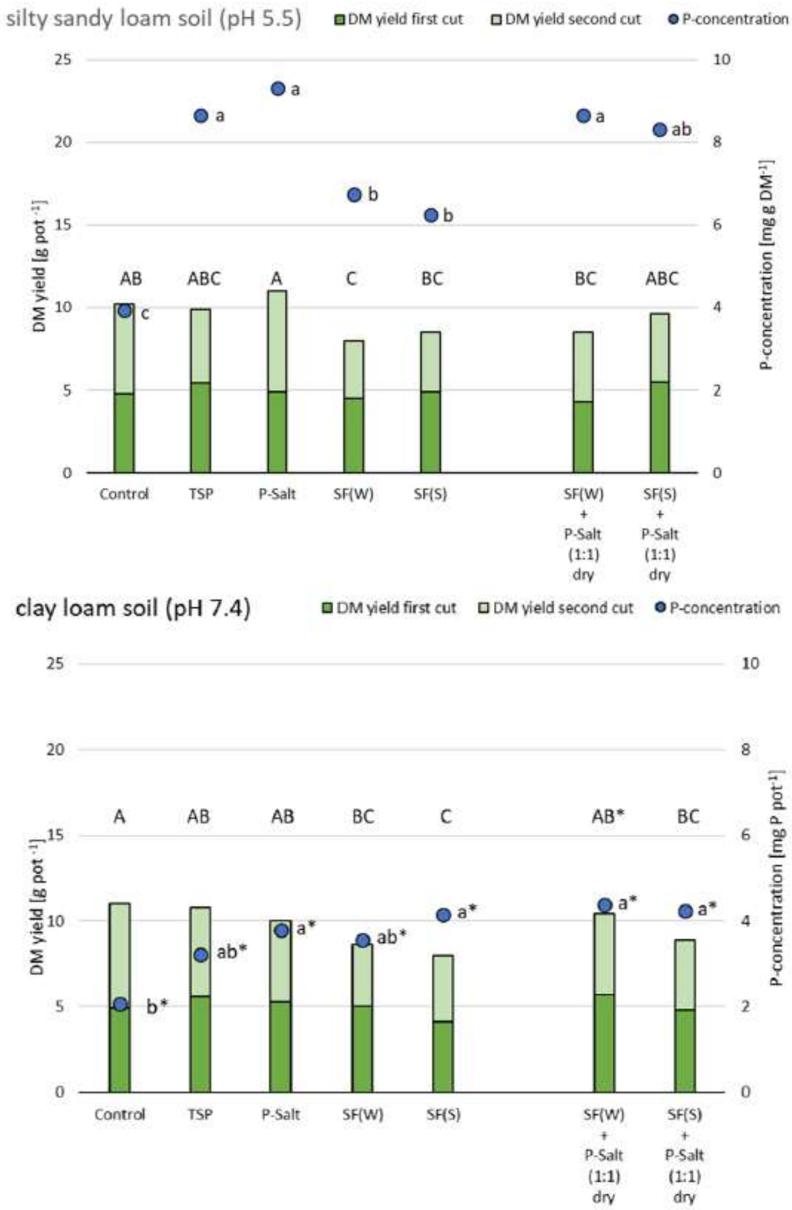

Figure 4. Total dry matter yield of ryegrass (DM yield) after 84 days in g pot^{-1}, separated into first and second harvest, and ryegrass P concentration in mg P/g DM after soil treatment with different recycled digestate fertilizers in a total dose equivalent of 150 mg P (kg soil)$^{-1}$; fractions tested: P-Salt, SF(W), SF(S), and two different combinations of them, compared to unfertilized control and TSP. Based on the total fertilizer dose corresponding to 150 mg P (kg soil)$^{-1}$, designation (1:1) means that fertilizers were applied with a mass portion of SF (W or S) containing 75 mg P (kg soil)$^{-1}$ + a mass portion of P-Salt containing 75 mg P (kg soil)$^{-1}$. Data are means of four replicates each. Different letters denote significant differences (two factorial Tukey test with $p \leq 0.05$), and significant differences between the soils are indicated by an asterisk (*).

In the acidic silty sandy loam soil, none of the P fertilizers increased DM yield significantly compared to the untreated controls, despite significant differences in the plant P concentration (see below). DM yield was the highest with P-Salt alone (11 g/pot) and lowest (around 8 g/pot) with both separately dosed solid fractions (SF(W) and SF(S)). Plants exposed to the combinations of P-Salt with SF(W) or SF(S) both gave yields between these extremes, indicating a slight suppressing effect of the solid fractions, confirmed also in comparison with the untreated controls that gave remarkably high yield, similar to TSP and P-Salt.

DM yield was not found to be correlated with P concentration. Plants grown in previously P-fertilized soil had P concentrations between 6 and 9 mg P/g DM, with the highest values after P-Salt treatment (9.3 mg P/g DM) and the lowest with both solid SF(W/S) treatments (ca. 6 mg P/g DM), which were still much higher than the untreated controls (3.9 mg P/g DM). Looking at both DM yield and P concentration together, the results indicate that plant uptake of P was increased by all P fertilizers; however, unlike in maize, it was without an associated increase of plant biomass.

In the neutral clay loam soil (pH 7.4), the highest DM yield (11 g/pot) was detected in the unfertilized controls, the TSP treatment group and one combination treatment (SF(S) + P-Salt). Overall, values were at the same level as in the acidic silty sandy loam soil. The combination treatment SF(S) + P-Salt and both solid fractions alone (SF(W/S) had the lowest, but still comparably high, DM yields (around 8 g/pot).

As expected, P concentration in ryegrass grown in the neutral clay loam soil was generally lower (3–4 mg P/pot) than in the acidic silty sandy loam (6–8 mg P/pot), ranging from 2.1 mg/g DM in the untreated controls to 4.4 mg/g DM in the SF(W) + P-Salt combination. Overall, P concentration in ryegrass, grown in this neutral soil, was rather inversely correlated with DM yield, at least with the single doses, indicating that P was not a limiting nutrient for this plant species in this experimental setup.

3.4. *Effect of P Fertilizers on Plant Nutrient Content in Ryegrass*

Similar to the maize experiment, the total P content per growth unit was related to the total plant biomass harvested per pot (Figure 5). In the acidic silty sandy loam, all P fertilizer treatments resulted in increased P content compared to the unfertilized controls. The highest P content was detected with P-Salt alone (102.4 mg P/pot). The TSP reference dosing gave slightly lower P content (85.7 mg P/pot). Both solid fractions (SF(W/S)) had the lowest P content of all fertilizer treatments (around 54 mg P/pot), which was still higher than the unfertilized controls. Intermediate P contents of ca. 75 mg P/pot were found after both combination treatments, SF(W/S) + P-Salt, where, in contrast to maize, values suggested rather additive than synergistic effects.

In the neutral clay loam soil, the total P content of all ryegrass harvests was 50–60% lower than in the acidic silty sandy loam soil. The highest P content in the neutral clay loam was detected with the combination treatment SF(W) + P-Salt (45.5 mg P/pot), with slight synergistic effects between the mixing partners. The second combination treatment (SF(S) + P-Salt) was on a similar level, and the effects were additive here. Of the single fertilizer treatments, TSP and P-Salt gave similar P contents of 34.7 and 37.9 mg P/pot, whereas both solid fractions (SF(W/S)) were slightly lower (30.5 and 33.2 mg P/pot). The lowest P-content (22.7 mg P/pot) was measured in the untreated controls.

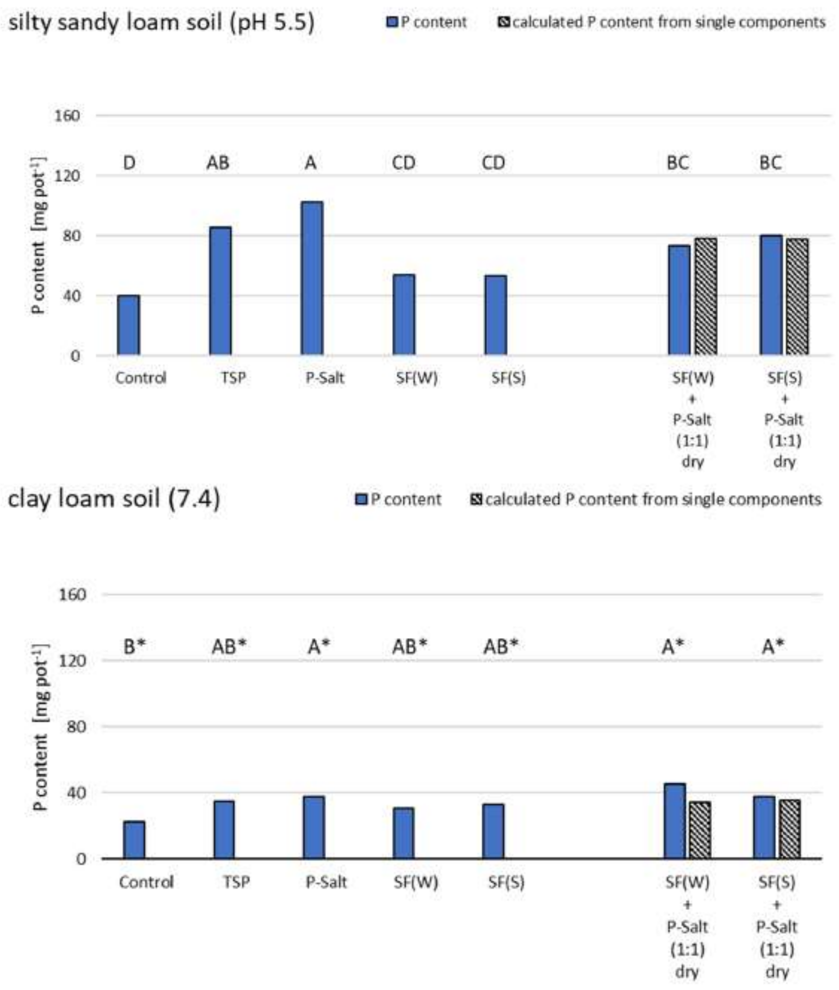

Figure 5. Total phosphorus content (P content) after 84 days in mg P/pot of ryegrass, initially treated with different recycled fertilizers in a total dose equivalent to 150 mg P (kg soil)$^{-1}$ followed by maize cultivation (50 days) and harvest; fractions tested: P-Salt, SF(W), SF(S), and two different combinations of them, compared to unfertilized control and TSP. Based on the total fertilizer dose corresponding to 150 mg P (kg soil)$^{-1}$, designation (1:1) means that fertilizers were applied with a mass portion of SF (W or S) containing 75 mg P (kg soil)$^{-1}$ + a mass portion of P-Salt containing 75 mg P (kg soil)$^{-1}$. Ryegrass plants were cultivated for 84 days, with a first harvest cut after 56 days, and a second cut after 84 days. Data are means of four replicates each. Different letters denote significant differences (two factorial Tukey-test with $p \leq 0.05$), and significant differences between the soils are indicated by an asterisk (*).

3.5. Effect of P Fertilizers on Plant Available P (CAL-P) in Soil

At the end of the experiment (134 days after soil fertilization, followed by maize cultivation for 50 days and harvest, and subsequent ryegrass cultivation for 84 days and harvest), the CAL-P concentration in the soil was analyzed as an indicator for the P plant availability as a function of the different initial P fertilizer treatments in both soils.

The results displayed in Table 2 show that all tested P fertilizers significantly increased the CAL-P concentration in the acidic silty sandy loam soil compared to the untreated control. The highest values were found in soil fertilized with P-Salt alone (81 mg P/kg soil), compared to only 19 mg P/kg soil in the untreated control (comparable to its initial value before fertilization of 15 mg/kg soil). P-Salt and both combinations with SF(S) and SF(W) resulted in higher CAL-P levels than the reference TSP, which was at the same level as the solids SF(S) and SF(W).

Table 2. CAL-extractable P (CAL-P) in soil.

P Sources	CAL-P after Ryegrass Harvest	CAL-P after Ryegrass Harvest
	Silty Sandy Loam Soil [mg kg^{-1}]	Clay Loam Soil [mg kg^{-1}]
Control	19 D	19 C
TSP	42 C	38 AB
P-Salt	81 A	44 AB *
SF(W)	50 BC	44 AB
SF(S)	43 C	33 B *
SF(W) + P-Salt (1:1) dry	61 B	43 AB *
SF(S) + P-Salt (1:1) dry	67 AB	48 A *

Plant available P (CAL-P) in mg (kg soil)$^{-1}$ after soil treatment with different recycled fertilizers in a total dose equivalent to 150 mg P (kg soil)$^{-1}$, maize cultivation for 50 days followed by ryegrass cultivation for 84 days; fractions tested: P-Salt, SF(W), SF(S), and two different combinations of them, compared to unfertilized control and TSP. Based on the total fertilizer dose corresponding to 150 mg P (kg soil)$^{-1}$, designation (1:1) means that fertilizers were applied with a mass portion of SF (W or S) containing 75 mg P (kg soil)$^{-1}$ + a mass portion of P-Salt containing 75 mg P (kg soil)$^{-1}$. Data are means of four replicates each. Different letters denote significant differences (two factorial Tukey-test with $p \leq 0.05$), and significant differences between the soils are indicated by an asterisk (*).

In the neutral clay loam soil, all tested P fertilizers also increased the free P concentration in soil compared to untreated controls (19 mg/kg soil; value prior to fertilization: 26 mg/kg soil), but to a lower extent than in the acidic silty sandy loam. Like in the acidic soil, P-Salt and both combination treatments gave higher values (43–57 mg/kg soil) than TSP (38 mg/kg soil). The highest CAL-P was found for SF(W), with 57 mg/kg soil.

4. Discussion

4.1. Effects of P Fertilizers on Maize Biomass Yield and P Uptake

Organic P fertilizers, produced from digestates of a biogas plant operating with a mixture of cow manure and maize silage, increased the dry matter yield of maize to the same or a higher extent than the reference triple superphosphate (TSP). Whilst the P fertilizing properties of this material have previously been investigated in neutral soils with different crops and soils [23,24,33], this study shows a comparison between a neutral clay loam soil (pH 7.4) and an acidic silty sandy loam soil (pH 5.5), both representing a large proportion of European agricultural soils [41].

Biomass yield in the neutral soil almost doubled compared to TSP when P-enriched salt (P-Salt), recovered from the liquid fraction of the digestate, or combinations with solid fractions were used. The increase compared to TSP was even more pronounced if compared to an earlier experiment performed with the same soil [23]. Combined treatments of P-Salt and solid fractions (SF(W/S)) generally gave equal or more favorable biomass growth compared to single treatments, with insignificant differences between the drying techniques of the recycled solids. The highest DM yield increase in the acidic soil was observed with combinations of P-Salt with solid fractions, and P-Salt alone had an effect similar to TSP. Apparently, P availability was less of a limiting factor in the acidic than in the neutral soil, which confirms earlier findings by [25]. The authors explained this effect by a higher abundance of $H_2PO_4^-$ over HPO_4^{2-} in soils with an acidic pH. While P-Salt had a higher relative influence on maize fertilization in the neutral soil, the solid fractions

(SF(W/S)), containing high proportions of organic material, apparently had a higher impact on DM yield increase under acidic soil conditions by an additional, yet unknown, growth stimulating mechanism.

Similar to earlier findings [23], P concentration in crops grown in the neutral clay loam soil was not significantly affected by any fertilization measure. However, total P content was positively correlated with DM yield across the different treatments, indicating that net P uptake into the plants increased with P-Salt and combinations. In contrast to the neutral soil, all fertilizer treatments increased the P concentration of crops grown in the acidic silty sandy loam soil by a factor of 2.5–5, but without direct correlation to DM yield. The net P uptake into the plants was the highest with P-Salt and combinations, and for the treatment combinations, this correlated well with their highest DM yield. The finding that soil pH has a great influence on P bioavailability was also reported earlier [31,42]. With respect to biomass increase, however, a comparison across all fertilizer combinations in both soils indicates that P uptake of plants in the acidic soil was beyond the limiting minimum for plant growth.

The influence of soil pH on the efficiency of recycled P fertilizer was investigated by [43], who used Magnesium-SSA. This material is a thermal recycling product from sewage sludge (sewage sludge ashes, SSA), which contains high amounts of Ca and Mg phosphates, similar to the P-Salt used in this study. The authors found that a high fertilizer efficiency of Mg-SAA was only observed under acidic (pH < 6.5) soil conditions. It was suggested that recycled P fertilizers might work best in acidic soils because the dissolution of Ca and Mg phosphates might be controlled by protons. Consequently, Möller et al. [42] recommended that Mg-SAA should be used under acidic soil conditions only. For the P fertilizer fractions in this study, however, it could be shown that the fertilizing effects in neutral soils were similar and even more pronounced than in acidic soils, so that the pH limitations observed earlier could be overcome with the material produced in the GOBi recycling process.

Summing up, the results described above confirm that P-Salt and combinations with the associated solid fractions can be effective alternative fertilizers to TSP for maize grown in neutral and acidic agricultural soils.

4.2. Influence of P Fertilizers on Ryegrass Biomass Yield and P Uptake

The DM yield of ryegrass, grown for 84 days in the remaining pots after previous maize cultivation, was not positively affected by any of the initial P fertilizations, neither in the acidic silty sandy loam soil nor in the neutral *clay loam* soil. P availability in both soils seemingly was not limited for ryegrass under these conditions of crop rotation, without additional P fertilization at sowing.

The absence of P fertilizing effects with ryegrass is in contrast to earlier findings by [44,45], who reported an increase of DM yield following P fertilizer application. Despite the difference that these authors used initial fertilization directly prior to cultivation, it was also mentioned by [45] that perennial ryegrass cultivated in warmer seasons at soil temperatures up to 13 °C did not show yield responses to P fertilizers and suggested that soil temperature may be a critical factor for ryegrass fertilization. The greenhouse pot cultivation in our study may be a model for summer season cultivation without observable P fertilizing effects. A more likely reason, however, is that the P concentration in both soils at the timepoint of ryegrass sowing still was above the maximum P demand of the plants.

Despite the biomass being unaffected by the fertilizer treatments, P concentration in ryegrass was increased compared to the untreated controls in both soils, and more so in plants grown in the acidic silty sandy loam soil than in the neutral clay loam. Ref. [46] reported that the optimum P concentration in plants is between 3.0–4.0 g/kg DM. Looking at the unfertilized vs. fertilized DM of ryegrass, sufficient P was apparently available in the neutral clay loam soil, and levels were even more than what was required in the acidic soil. Ryegrass is known to extract P from soils; the application of P fertilizer has led to an accumulation of total soil P and is therefore a good candidate for phytoremediation in many agricultural soils [47], reducing the risk of P loss to the environment. The results of this study show that P extraction by ryegrass is also possible after use of recycled P fertilizers. Our finding that the P concentration in ryegrass plants was much higher compared to maize plants is in line with earlier reports (for maize, e.g., [48,49]; for ryegrass, e.g., [44]).

4.3. CAL-P in Soil

The measured CAL-P concentration in both soils, 134 days after P fertilization and growth of maize and ryegrass, was still increased with all tested P fertilizers compared to the untreated control. CAL-P, representing the P pool available for plant uptake over time, was generally lower in the neutral clay loam soil (pH 7.4) than in the acidic silty sandy loam soil (pH 5.5). This confirms once more that increased soil pH towards neutral or slightly alkaline conditions causes a decrease in soluble P or an increase in P sorption and/or P immobilization [50], so that plant-available P may become suboptimal for crop production, although total soil P is high [49]. In contrast to the neutral soil, the acidic silty sandy loam soil had most likely fewer binding sites for P and a higher P mobilization potential, which allowed for higher P uptake in maize and ryegrass plants.

The highest CAL-P concentrations were observed in the acidic soil treated with P-Salt alone or in combination with the recycled solids, which correlates with the increased net uptake of P into the plants. In the neutral soil, no clear difference between the P fertilizer treatments could be observed for CAL-P, which is again in line with the low P concentration in both plant species compared to the acidic soil. Unlike in the study by Bach et al. [23], correlations between CAL-P and DM yield could not be observed here, even in the same neutral clay loam soil used in this study. However, CAL-P was measured much later here than in the previous setup and might be dependent on the temporary soil/rhizosphere–plant continuum [4,51].

5. Conclusions

In the present study, we compared P fertilizers recovered from digestates of a biogas plant, operating with a mixture of cow manure and maize silage, in two different soils and plant species. Compared to the reference fertilizer TSP, the recycled fractions tested alone or in combination caused similar or even higher DM yield in maize plants cultivated in soils with neutral as well as with acidic pH. In contrast to this, ryegrass biomass was not increased by any P fertilization treatment in both soils, which might be an important finding for grassland cultivation and weed management in maize or other crops. Despite biomass production being unaffected by all P fertilizers, an increased net uptake of P in ryegrass represents an option to extract excess P from soils after treatment with the recycled fertilizers used in this study.

Significant differences were observed for P concentration and total P content in both maize and ryegrass plants, with the acidic silty sandy loam soil and the neutral clay loam soil, suggesting possible fertilization regimes for soils with different pH in agricultural practice.

The results of this study show that the recycled P fertilizers investigated have a high potential for replacement of inorganic P derived from phosphate rock, not only in neutral but also in acidic soils. Our investigations were run as pot experiments under controlled greenhouse conditions. Investigations under field conditions, including further research on the associated soil/rhizosphere interactions, like phosphatase activity, plant growth–promoting rhizobacteria, release of organic acid anions and more, will be important to understand the underlying effects and influencing parameters that are essential for commercial use in maize growth and other agricultural circumstances.

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6 General Discussion

6.1 The concept of digestate recycling

The recycling of P from its accelerated anthropogenic use is one of the big challenges in modern economy. Naturally available P resources on earth are limited to only a few hundred years and an excess of P in the environment causes increasing environmental stress and loss by dilution. Recycling of P starts with the identification of the major material flows, followed by the development of suitable recycling technology, the investigation of the fertilizing properties of the recycled material and finally ends with the technical realization on a large scale. Closing loops in crop and animal production, that account for the by far highest P consumption worldwide, has therefore been in focus of many investigations in the last years.

Recycling of livestock manure on agricultural land is probably one of the oldest recycling concepts in agriculture, still used successfully in many situations. Manure contains valuable plant nutrients, maintains soil fertility, and substitutes mineral fertilizer. Main issues with direct application besides odor nuisance are the partial loss of nutrients into the atmosphere, the potential contamination of groundwater, especially with nitrate, high energy costs for storage, transport and application, and potential accumulation of toxic by-products like heavy metals in soil. In the last 15-20 years, detailed legislation was enacted by the EU and its member states to ensure that negative side effects of manure use in agriculture are minimized.

In areas with high livestock density, the direct application of animal manure to agricultural land has become impossible without strict regulation of its temporal and spatial distribution, and agricultural land has become subject of a “nutrient exchange market” (german: Nährstoffbörse) for manure “disposal”. Along with the public attention to the reduction of global warming, energy transition and renewable energies, modern legislation encouraged technologies for biofuels and biogas production, and thereby opened opportunities for the alternative use of manure as substrate in biogas plants.

The digestate of biogas plants contains high amounts of inorganic and organic nutrients and is consequently used as soil fertilizer by direct application. The advantages over direct manure application are reduced odor, pathogen levels and greenhouse gas emissions (Sárvári Horváth, 2016). However, the other disadvantages, described above for unprocessed manure, remain. Research on technologies to overcome these disadvantages has focused recently on the production of a stable, defined quality, the reduction of the large volumes, and an optimized fertilizing efficiency of the resulting material. The most striking benefits of a digestate upgrade are the reduction of costs for storage, transport and application and the increase of flexibility of use compared to the raw digestate. Storage capacity of high-volume manure can be reduced during the wintertime when field application is mostly prohibited. With drastically reduced water and increased nutrient content, fewer application events are needed, leading to reduced energy consumption and less disturbance of the field soil structure. Additional added value comes from the potential to create more target-oriented fertilizer regimes by the combination of different mixing partners tailored to the agronomic situation. Also, processing opens the possibility to control unwanted, potentially harmful or toxic trace elements and the production of a defined quality of recycled fertilizers.

Typical substrates for processing are digestates from pig, cattle, and chicken manure in co-digestion with food waste, energy crops and agricultural straw (Shi et al., 2018). Different technical approaches for P recycling from biogas digestates have been developed, like adsorption and ion exchange, membrane separation, thermal treatment, and chemical precipitation. The challenge of precipitation is to create conditions for a balanced counter ion milieu between competing cations (Ca, Mg, Na, K, NH_4) and PO_4^{3-} in order to facilitate the formation of P salt complexes. Conditions have to be robust against varying substrate ion concentrations and should avoid formation of high levels of insoluble calcium phosphate. The supplement of Mg^{2+} as MgOH, $MgCl_2$ or $MgSO_4$, together with pH control, are key factors in this process. The struvite precipitation recovers both N and P from digestates and is one of the most popular technologies. The fertilizer effect of struvite was reported to be similar as that of TSP and also has slow release properties in practical use (Römer and Steingrobe, 2018).

The recycled material used in this work originated from a pilot plant in southern Germany designed for combined biogas production and P-recycling. The capacity of the pilot plant was 100 kg of digestate per hour to about 1 kg of mineral phosphorus fertilizer, 1 kg of mineral nitrogen fertilizer as well as 1.8 kg of organic solid fraction (Vorbeck, 2016). The first recycled product was Phosphate Salt ("P-Salt"), precipitated from the liquid fraction of the digestate after solubilization, that contained struvite besides other salt complexes. The second product was a solid fraction ("SF") that was concentrated by different drying methods, from low-temperature air drying over steam drying to pyrolysis. A newest press (Rudolph, 2020) released from 2020 titled, that the next step from pilot plant to the construction of six large-scale facilities with a capacity of 150.000 m^3/h in sum was in the planning phase. The building construction of the first large-scale facility was scheduled to start in 2021 with the others following in due course (Rudolph, 2020).

The series of investigations presented here centers around the biological efficiency of recycled Phosphate Salt ("P-Salt") and its related byproducts (solid fractions, "SF") under controlled, repeatable, and comparable greenhouse conditions as models for agricultural use. The results of investigations with the recycled fractions of the GOBi project are summarized in the following paragraphs.

6.2 P fertilization efficiency of fractions recycled from biogas digestates

6.2.1 General Overview

The studies presented in Chapter 2-5 with different agricultural crops and ornamentals demonstrate that P fertilizers recycled from biogas digestates have a high potential as substitute for conventional mineral P fertilizer (TSP). Indicators for fertilization efficiency of the tested recycled P fertilizers and its combinations in the studies of this thesis were plant dry matter yield, plant P concentration and content, and CAL-P in soil, all compared to a conventional triple superphosphate (TSP) and untreated controls. Effects in a range of different soils (low/high pH, nutrient-rich/ nutrient poor) and plants (crops, ornamentals, grass) were robustly equal or even stronger than conventional triple superphosphate (TSP). Differences in P fertilization efficiency was observed with single application compared to combinations of different fractions.

The studies confirm that different plant species react differently to P fertilization in general, and thus also to recycled P fertilizers. The response to TSP as well as recycled P fertilizer was highest in maize and barley, and moderate but significant in broad beans, Chinese cabbage, and sunflower. Marigold and ryegrass, however, did not display a significant increase of biomass with either of the P fertilizers when compared to untreated controls. Still, P concentration in plants had also increased in these species. Hypothesis H_7 was thereby confirmed.

6.2.2 P-Salt fertilization vs. TSP

The fertilizing performance of P-Salt alone was investigated in comparison to equivalent amounts of TSP in different crop-soil-combinations in greenhouse pot experiments of this thesis. In all evaluated crop situations, dry matter yield (DMY) increase was equal or higher compared to TSP for barley, maize, broad beans, Chinese cabbage, and sunflower, thus confirming hypothesis H_1.

P concentration and total P content in the shoots increased after P fertilization in all cases and again effects were similar between P-Salt and TSP in all investigated plant species (confirmation of hypothesis H_6).

A special case is the comparison of P-Salt derived directly from manure in comparison to P-Salt from biogas digestate, described in Ehmann and Bach (2018). Differences between both tested P-Salts were generally low, indicating that the recycling process was robust to the different input substrates with respect to fertilizing effects in different plants.

6.2.3 Solid fractions as single application

Two solid fractions, prepared by air-drying and steam-drying, were compared in single application to different crops and soils. In maize and sunflower, where significant DMY increase was detected after all P fertilization treatments, both solid fractions displayed fertilizing properties similar to TSP and P-Salt in neutral soils, and even higher efficiency in one acidic soil. Since the solid fractions contained organic material in addition to P, it is likely that the DMY increase was also triggered by different processes that can be summarized as soil conditioning properties. Shinde et al. (2019) defined soil conditioners as any material with limited amount of nutrients that has a beneficial impact on the biological, physical or chemical nature of soils. In the case of steam dried solids, rather physical and chemical influences rather than microbial activity may have contributed to the conditioning effects, since steam drying is likely to have eliminated any microbial activity (Scherer et al., 2020). Overall, data confirmed hypothesis H_2.

Similar to P-Salt alone, the uptake of P into plants was increased by the solid fractions in sunflower, marigold, Chinese cabbage, ryegrass and maize when compared to untreated controls. The effect was more pronounced in one acidic soil with maize. Even though plant growth was not increased in all plant species, the higher concentrations of P in the plants indicate that the solids favored P transport into the plant in all cases investigated.

Across all soils and crops tested, steam-dried solids resulted in slightly higher DMY increase than air-dried solids. (Ehmann and Bach, 2018; Bach et al., 2021; Bach et al., 2022) Steam drying is a well-established process in the food industry (van Deventer and Heijmans, 2001). Energy input for steam drying is more efficient than air-drying, and advantages are that the drying process is faster and results in a more homogeneous material with high surface to volume ratio. Furthermore, oxidative processes are minimized, and simultaneous sterilization/pasteurization is possible. Hypothesis H_4, predicting a difference between drying technologies of the solids, was thus confirmed.

6.2.4 Treatment combinations of P-Salt and solid fractions

Earlier findings had indicated that biochar addition to mineral fertilizer enhanced crop yield (Schulz and Glaser, 2012) and the results of Ehmann et al. (2017). confirmed that DM fractions, pyrolyzed to biochar, enhanced the efficiency of P-Salt when applied in combination. Small additions of biochar slightly increased DMY in barley and broad beans in a sand and a clay soil. Due to the relatively low fertilization enhancement effect of biochar and a high energy input needed for pyrolysis, the focus in the following studies was set on a more conservative treatment of the solids in order to maintain their biological and mechanical properties with a reduced energy input. This was realized by using air-dried solids and steam-dried solids, prepared in the GOBi pilot plant.

Combinations of air-dried solids with P-Salt were investigated by Ehmann and Bach et al. (2018) in a slightly acidic soil. Bach et al (2021, 2022) compared combinations of both, air-dried and steam-dried solids with P-Salt. Strong synergistic effects were observed between P-Salt and solids with a nutrient-poor and microbially depleted subsoil and another nutrient-poor, acidic surface soil. In a third soil, a surface soil with neutral pH and moderate microbial activity, effects were rather additive. In no case, antagonistic effects between P-Salt and solid fractions could be observed, so that hypothesis H_3 was confirmed. Even though the underlying processes are not understood in detail, it can be reasonably concluded that microbial activity, pH and organic matter supply are major factors of the soil conditioning effect of the solids used in these studies, a concept that was also investigated by Risberg et al. (2017) and Brod et al. (2015). The results with the combinations also indicate that soil specific mixing partners for P-Salt can be found for an optimized P fertilization regime, and that in the absence of clear predictors, it is advisable to experimentally investigate this optimum in the field. Besides the investigation of the correct ratio, mixing methods, as investigated in Bach et al. (2021, 2022), apparently also influence fertilizer effects and are another subject for individual adaptations.

6.2.5 Soil type, pH and CAL-P

Penn et al. (2019) gave a critical review of the importance of soil pH for nutrient availability to plants. The authors stated that pH has a profound impact on many factors other than P solubility, that influence plant growth over time and concluded that a soil pH near 6.5 is a robust target for maximum P availability.

The influence of soil pH on the investigated P fertilizers was reported by Bach et al. (2022), who used P-Salt and solid fractions in different combinations in two soils with different pH in maize as a model for a highly P sensitive plant. P-Salt alone gave highest DMY increase in the neutral soil, whereas highest values in the acidic soil were found with solids alone. The combination of both fractions, however, resulted in comparable DMY in both soils, superior to TSP in both cases. Johan et al. (2021) described that decomposition of organic matter causes soil acidification by dissociating their carboxylic, enolic and phenolic groups and release of H^+. An acidification of the solids during decomposition might explain the increase of soluble P in the soil as a secondary pH effect. Since fertilization efficiency varied between soils with different pH and soil type, hypothesis H_5 could be confirmed. For practical use, this means that the pH related strengths of P-Salt and solids can be played with the right mixing proportion dependent on the soil pH.

CAL-P, representing the soil P pool available for plant uptake, was lowest in unfertilized controls compared to any fertilization measures in all investigated soils and plant species. P-Salt and solids significantly increased CAL-P in all soils, confirming hypothesis H_8. These results are in accordance with the P concentration and P content findings in different plants shoots. Despite different growth effects of the recycled fertilizers, this shows that the availability of P in soil and plants was positively influenced with the recycled fertilizers in all soils and plants. In conclusion, the measurements of CAL-P in soil and P concentration in plants underline that P availability to plants is positively influenced by the use of the investigated P fertilizers regardless of growth effects which were not observed in some plants (marigold, Chinese cabbage, ryegrass).

6.3 Management of recycled P fertilizers in agricultural practice

The call for more sustainability in agriculture in recent years causes an increased interest of society in closing nutrient cycles throughout the agri-food chain. For a reduction of mineral fertilizer input, the improvement of nutrient recycling and the development of economical and efficient fertilizers is a key factor. However, biobased fertilizers are challenging due to their more complex dynamics, making their use more difficult to predict and to plan as for mineral fertilizers.

Main issues to be considered when using recycling P fertilizers are (1) initial nutrient status of the surface and subsoil, (2) soil pH, microbial activity and organic matter status (Schröder 2011), (3) crop specific fertilizer need, (4) local climate and hydrology (5) timing of fertilizer supply, and (6) selection of the appropriate fertilizer combinations (Garske et al., 2019). P fertilizers should not be oversupplied or be reduced to a level below the plant optimum, to avoid P losses to the environment and suboptimal supply. The risk of soil erosion by water and wind and in consequence the risk of P losses into waterbodies should be avoided where possible by farmers through conservative tillage methods. Soils with high bound P may require the use of crops with efficient P uptake properties in order to reduce environmental pressure of P oversupply.

6.4 Recycled P fertilizers on the marketplace

One of the innovative principles of recent legislation for recycled fertilizers is their recognition as products rather than waste. Product specification and labeling of recycled fertilizers makes them available to the general fertilizer market. With this principle, a value is assigned to the recycled fertilizer and economical assessment of product generation is possible. This value can take into account savings from manure management upstream of the recycling process, transport logistic costs and possible reductions of environmental pressure of the direct use of unprocessed manure. An indicator for this development is the recent acquisition of a patent for digestate recycling by a leading German recycling company (Rudolph, 2020; Mahr, 2019). Politics and society can then decide to what extent the product prices on the open market shall be regulated in favor of sustainable, recycled fertilizers.

6.5 Future needs for realization

The presented data of the investigated studies demonstrate an obvious benefit by using recycled P fertilizer products from biogas digestates or manure on different soil and plant conditions. The results of these experiments performed under greenhouse conditions will need to be confirmed in the field at varying soil-climate conditions. In addition, experiments with additional commercial crops can open more possibilities for the use and complete the applicability of P recycled fertilizers. Crop rotation, tillage, and additional agronomic measures in the filed may also influence the efficiency of P fertilization. Since P-Salt revealed very similar properties to TSP in all experiments, focus should be set on the recycled solids of which knowledge on composition and processes is still limited.

In one of the studies (Bach et al., 2021), different mixing techniques were investigated (pre-mixing with water or direct application of the dry material to soil). Slightly different effects were found in this investigation and no longer followed, but the results make it likely that application techniques, also others than investigated, may influence P fertilization efficiency under field conditions.

Another point of interest is certainly the N fraction of the GOBi recycling process. Nitrogen and Phosphor are the two main and most essential nutrients to ensure food production. They closely interact between each other and may modulate plant nutrition (Ohkama-Ohtsu and Wasaki, 2010), for example via upregulating the active transport system for inorganic N and P uptake. Characterization, use, fertilization efficiency and interaction with P and other fertilizers will be of interest to evaluate if recycled N fractions can have similar properties to inorganic N used in conventional agriculture.

As mentioned above, little is known about the biological composition and functional properties of the solid fractions prepared by air-and steam drying in the recycling process. Their characterization as “soil conditioners” is an assumption that is not finally proven. Apparently, steam-drying resulted in a product superior to air-drying, but a detailed understanding of the underlying physiology and mechanics is still needed. One of the factors may be the enzyme activity in soil that strongly influences soil mineralization processes. Recently, also soil bioeffectors were investigated for their supportive potential to mobilize nutrients for improved plant uptake (Nkebiwe, 2016), representing elements that can complete farmers’ toolbox for soil and crop management.

As mentioned above, the transition of recycled material from waste to a labelled product requires a detailed financial analysis for a commercial use. Companies with experience in the recycling market qualify best for the assessment of investments, input and output. Part of this is the analysis of the upstream savings from reduced storage logistics, overcoming seasonal application restrictions, and obsolete application effort for the raw manure, that may all be regarded as monetary benefits. Together with the downstream side of the calculation, represented by the cost comparison with TSP products, a total economical balance dependent on the scale of the biogas plant can be generated.

For a holistic view, society and politics ultimately expect a complete financial and ecological balance for the entire recycling process for an objective scientific assessment of the compatibility of all its elements with sustainability goals. This will be an iterative, ideally real-time effort that takes into account existing and updated new scientific findings.

7 Conclusion and outlook

In this thesis, P fertilizers recycled from biogas plant digestates were chemically characterized and tested for their biological efficiency in different crops and soils, alone or in combination, always in comparison to the mineral fertilizer TSP and unfertilized controls, under controlled greenhouse conditions. The P-Salt fraction, a precipitate of P-rich minerals from the liquid fraction of the digestate, had almost identical properties to TSP. Fractions derived from two different substrates (pig manure and cow/maize digestate) gave similar results. The solid fractions, still containing P and other elements in a lower concentration but mainly constituted of organic material, had additive or even synergistic effects on P fertilization, and sometimes were effective as fertilizers themselves. Steam-drying was the superior drying method for the solids. Differences were found between soils, mostly influenced by their pH, organic matter, and microbial activity. The P influenced increase of biomass was different in different crops, but similar between TSP and recycled fractions. P uptake and concentration in plants was generally in the same order of magnitude compared to TSP.

The recycling economy between plant and animal production as the dominant anthropogenic material flow of P has been improved by technology in recent years. It is now possible to extract residual energy and purified, defined fertilizers from manure, and to reduce uncontrolled release of unwanted materials into the environment. The recycled fractions from manure and biogas digestates have the potential to be used in the field as alternative P fertilizers, substituting TSP in a wide range of crops and soils, and reducing the input of mineral PR in the future. Further to the fertilizer properties presented in this thesis, the practical use under field conditions remains to be investigated. A refined ecological safety assessment, especially in soil, and an economic evaluation of the entire recycling process are proposed as next steps to apply this technology on a large scale.

8 Summary

Phosphor (P) supply to plants is a key production factor for quantity and quality of food in agriculture. P consumption in modern agriculture has increased with raising world population. Mineral P fertilizer derived from Phosphate Rock (PR) mines is a limited resource on earth and large amounts of P used in agriculture are diluted by distribution into the environment, causing unwanted environmental side effects. Future oriented use of P therefore has to be based on technologies for P-recycling from the main anthropogenic product streams.

In this thesis, P recycling products from a pilot plant were investigated for their biological efficiency as fertilizer in comparison to a conventional mineral fertilizer triple superphosphate (TSP). Investigations were part of two research projects (BioEcosim & GOBi) that had the goal to develop scalable technology for a sustainable P recycling in agriculture. Inputs into the pilot plant were unprocessed pig manure, and on the other hand a biogas co-digestate from cow manure and maize. Outputs were salt precipitates (P-Salt) from the separated liquid fractions with high P content, and solid fractions dried by pyrolysis, air-drying or steam-drying with moderate P content and high organic carbon.

The objective of the work described here was the biological and agronomical investigation of the recycled fertilizer fractions for their potential to substitute a mineral fertilizer.

In a first step, the obtained fractions were chemically characterized for basic characteristics. Based on the P content of the recycled fertilizers, greenhouse pot experiments were set up to compare equivalent P concentrations of single doses and combinations, in different crops and soils, with TSP and an unfertilized control as reference. Fertilizers were applied once before the beginning of the vegetation phase at recommended field rates. Variables investigated were above ground plant biomass production, concentration, and content of P in shoots, and plant-available P in soil.

The characterization of the precipitated P rich fractions revealed that the composition of the P bound minerals was a mixture of magnesium ammonium phosphate (struvite) and calcium phosphates. Their total P content (circa 110 g/kg DM) was slightly lower than TSP (190 g/kg). The organic solids contained lower (circa 20 g/kg) but still significant amounts of P. All fractions displayed a slightly alkaline pH in $CaCl_2$, between 7 and 8.5.

In all experiments, single dosing with the recycled P-Salt fractions resulted in fertilizer effects on biomass growth similar or higher than the reference TSP. This result was found in all soils and crops investigated, indicating that the recycled P-Salt was an effective substitute for TSP. Under the conditions tested, three of the investigated crops, namely marigold, Chinese cabbage and ryegrass, did not develop P induced biomass increase at all, probably because the relevant growth phases were not covered or because the initial P concentrations in soil were already equal or above the optimum P concentration in soil. Highest effects were found in maize, a typical input crop for biogas plants.

The single dosing of the isolated solid fractions in two acidic soils, using maize and sunflower, resulted in an even higher biomass increase compared to TSP and P-Salt, whereas effects were generally lower in neutral soils. Steam-dried solids showed a tendency to be superior to air-dried and pyrolyzed solids.

When some combinations of solids with P-Salt were applied, biomass increased to an extent equal or higher than P-Salt or TSP alone. Effects were partly synergistic or additive, but never antagonistic. Different mixing techniques investigated resulted in only small differences in biomass increase.

A fertilizer induced increase of P concentration or content in the above ground plant biomass, dependent on the plant growth rate, was found in almost every tested crop. The results indicate that uptake of P from soil treated with recycled fertilizers occurred to the same extent than with TSP, independent from the individual growth rate.

Plant available P in soil, detected as CAL-P, was increased by all fertilizer fractions compared to untreated controls. This suggests that the chemical composition of the recycled P fertilizers was favorable for a high release of plant available P in soil and underlines the high technical quality of the established manufacturing processes.

Overall, the results indicate that P fertilizers recycled from unprocessed manure or biogas plant digestates can be used as an adequate substitute for mineral P fertilizer in a range of different crops and soils.

Confirmation of the results in the field and adoption to actual crop-soil-climate situations will be needed for practical use in agriculture. A detailed sustainability evaluation, taking into account all input and output parameters, will help to assess the practical use, applicability and value of the described recycling process.

9 Zusammenfassung

Die Versorgung von Pflanzen mit Phosphor (P) ist ein wesentlicher Produktionsfaktor für die Quantität und Qualität von Nahrungsmitteln in der Landwirtschaft. Der P-Verbrauch in der modernen Landwirtschaft hat mit steigender Weltbevölkerung zugenommen. Mineralischer P-Dünger aus natürlich vorkommenden Phosphat-Erzen (engl. Phosphate Rock, PR) ist eine global begrenzte Ressource und große Mengen des in der Landwirtschaft verwendeten P werden in die Umwelt ausverdünnt, was zu unerwünschten Nebenwirkungen in der Umwelt führt. Eine zukunftsorientierte Verwendung von P muss daher auf Technologien zum P-Recycling aus den wichtigsten anthropogenen Produktströmen basieren.

In dieser Arbeit wurden P-Recyclingprodukte aus einer Pilotanlage auf ihre biologische Effizienz als Dünger im Vergleich zu einem konventionellen Mineraldünger Triple superphosphat (TSP) untersucht. Die Untersuchungen waren Teil zweier Forschungsprojekte (BioEcosim & GOBi), die zum Ziel hatten, skalierbare Technologien für ein nachhaltiges P-Recycling in der Landwirtschaft zu entwickeln. Inputs in die Pilotanlage waren einerseits unverarbeiteter Schweinedung, und zum anderen ein Biogas-Gärrest aus Kuhdung und Mais. Outputs waren Salz-Präzipitate (P-Salz) aus den abgetrennten flüssigen Fraktionen mit hohem P-Gehalt, sowie mittels Pyrolyse, Lufttrocknung oder Dampftrocknung getrocknete, feste Fraktionen mit mäßigem P-Gehalt und hohem organischem Kohlenstoff.

Ziel der hier beschriebenen Arbeiten war die biologische und agronomische Untersuchung der recycelten Düngemittelfraktionen auf deren Potential, als Ersatz eines Mineraldüngers dienen zu können.

In einem ersten Schritt wurden die erhaltenen Fraktionen chemisch auf grundlegende Kenngrößen charakterisiert. Basierend auf den Ergebnissen des P-Gehalts der recycelten Düngemittel wurden Topfexperimente im Gewächshaus durchgeführt, um äquivalente P-Konzentrationen von Einzeldosen und Kombinationen in verschiedenen Kulturen und Böden mit TSP und einer ungedüngten Kontrolle als Referenz zu vergleichen. Düngemittel wurden einmalig vor Beginn der Vegetationsphase in empfohlenen Feldmengen ausgebracht. Untersuchte Variablen waren die Produktion von Pflanzenbiomasse, Konzentration und Gehalt von P im Spross und pflanzenverfügbares P im Boden.

Die Charakterisierung der ausgefällten, P-reichen Fraktionen ergab, dass die Zusammensetzung der P-gebundenen Mineralien eine Mischung aus Magnesium-Ammonium-Phosphat (Struvit) und Calcium-Phosphaten war. Ihr Gesamt-P-Gehalt (ca. 110 g/kg Trockenmasse (TM)) war etwas niedriger als der von TSP (190 g/kg). Die organischen Feststoffe enthielten geringere (ca. 20 g/kg TM), aber immer noch signifikante Mengen an P. Alle Fraktionen zeigten einen leicht alkalischen pH-Wert in $CaCl_2$ zwischen 7 und 8,5.

In allen Experimenten führte die Einzeldosierung mit den recycelten P-Salz-Fraktionen zu Düngemitteleffekten auf das Biomassewachstum, die ähnlich oder höher waren als die der Referenz TSP. Dieses Ergebnis wurde in allen untersuchten Böden und Kulturen gefunden, was darauf hindeutet, dass das recycelte P-Salz ein wirksamer Ersatz für TSP war. Unter den getesteten Bedingungen entwickelten drei der untersuchten Kulturpflanzen, nämlich Ringelblume, Chinakohl und Weidelgras, überhaupt keinen P-induzierten Biomasseanstieg, wahrscheinlich weil die relevanten Wachstumsphasen nicht abgedeckt wurden oder die im Boden vorhandene Initialkonzentration schon im oder über dem Optimum lag. Die stärksten Effekte wurden bei Mais, einer typischen Input-Kultur für Biogasanlagen, festgestellt.

Die einmalige Dosierung der isolierten Feststoff-Fraktionen in zwei sauren Böden unter Mais und Sonnenblumen führte zu einer noch höheren Biomassezunahme im Vergleich zu TSP und P-Salz, während die Effekte in neutralen Böden im Allgemeinen geringer waren. Dampfgetrocknete Feststoffe zeigten tendenziell höhere Effekte im Vergleich zu luftgetrockneten und pyrolysierten Feststoff-Fraktionen.

Bei der Applikation von einigen Kombinationen von Feststoffen mit P-Salz nahm die Biomasse in einem Ausmaß zu, das vergleichbar oder höher war als das von P-Salz oder TSP allein. Die Effekte waren teilweise synergistisch oder additiv, aber nie antagonistisch. Unterschiedliche untersuchte Mischtechniken ergaben nur geringe Unterschiede in der Biomassezunahme.

Ein durch Dünger induzierter Anstieg der P-Konzentration bzw. des P-Gehalts in der oberirdischen Pflanzen-Biomasse, abhängig von der Pflanzenwachstumsrate, wurde bei fast allen untersuchten Kulturpflanzen festgestellt. Die Ergebnisse deuten darauf hin, dass die Aufnahme von P aus mit Recyclingdünger behandelten Böden unabhängig von der individuellen Wachstumsrate im gleichen Ausmaß erfolgte wie bei TSP.

Pflanzenverfügbares P im Boden, nachgewiesen als CAL-P, war durch alle Düngemittelfraktionen im Vergleich zu unbehandelten Kontrollen erhöht. Dies legt nahe, dass die chemische Zusammensetzung der recycelten P-Düngemittel eine hohe Freisetzung von pflanzenverfügbarem P im Boden begünstigt und unterstreicht die hohe technische Qualität der etablierten Herstellungsverfahren.

Die Ergebnisse zeigen, dass P-Düngemittel, die aus unverarbeitetem Dung oder Biogasanlagen-Gärresten recycelt werden, als adäquater Ersatz für mineralischen P-Dünger in einer Reihe verschiedener Kulturen und Böden verwendet werden können.

Für den praktischen Einsatz in der Landwirtschaft ist eine Bestätigung der Ergebnisse im Feld und eine Anpassung an die tatsächlichen Pflanzen-Boden-Klima-Situationen erforderlich. Eine detaillierte Nachhaltigkeitsbewertung unter Berücksichtigung aller Input- und Output Parameter wird dabei hilfreich sein, den praktischen Nutzen, die Anwendbarkeit und den Wert des beschriebenen Recyclingverfahrens zu beurteilen.

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11 Curriculum Vitae

Personal Information

Name	Inga-Mareike Bach
Date and place of birth	August 31, 1988 in Hanover

Education

10.2013 – 07.2022	**Doctoral studies** Fertilization and Soil Matter Dynamics (340i) University of Hohenheim, 70599 Stuttgart (GER) Dissertation: “Characterization of phosphate fertilizers recycled from biogas digestates and their influence on plants-soil fertility indicators”
10.2011 – 09.2013	**Master of Horticulture Science** Institute of Plant Nutrition Leibniz University of Hannover, 30599 Hannover (GER). Master thesis: “Sulfur-enhanced plant defence against Verticillium dahliae in a tomato introgression-line population”
10.2008 – 10.2011	**Bachelor of Horticulture Science** Institute of Plant Nutrition Leibniz University of Hannover, 30599 Hannover (GER). Bachelor thesis: “ Validierung eines absoluten qRT-PCR-Tests zur Quantifizierung des Verticillium dahliae Befalls von Tomatenintrogressionslinien”
06.2008	**school examination (German Abitur)** Hölty-Gymnasium, 31515 Wunstorf (GER)

Employment history

09.2017 – today	**Business Development Manager** SGS INSTITUT FRESENIUS GmbH – Health & Nutrition, 65232 Taunusstein (GER)
09.2016 – 01.2017	**Fertilization assessment assistant** ASB Grünland Helmut Aurenz GmbH 70499 Stuttgart (GER)
09.2014 – 01.2017	**Research assistant** University of Applied Science (HfWU), 72622 Nürtingen (GER)
03.2011 – 09.2013	**Research assistant** Institute of Plant Nutrition Leibniz University of Hanover, 30599 Hanover (GER)

Practical experience

Workshops	**8th International Phosphorus Workshop,** Rostock (GER) (12.-16.09.2016)
	International Workshop of the German Society of Plant Nutrition (DGP), Bonn (GER) (5. - 8.09.2012)
Advanced Training	**Trainer / Instructor's Aptitude Qualification Course** (Ausbildereignungsprüfung nach BGBI.I.S.88), University of Hohenheim, 70599 Stuttgart (GER), examination passed on 07.2016
Internship	**Practical work experience in horticulture** Anzuchtgärtnerei im Nettoregiebetrieb der Herrenhäuser Gärten, 30419 Hannover (GER) (08.2010 – 09.2010)

Special Skills

Computer/IT	**MS Office** word, excel, power point **Statistical software** SAS, SigmaStat, R **Enterprise resource planning software** SAP
Languages	German, English (B 2.2)

Articles (peer-reviewed)

Ehmann, A., **Bach, I.-M.**, Laopeamthong, S., Bilbao, J., Lewandowski, I. (2017): Can Phosphate Salts Recovered from Manure Replace Conventional Phosphate Fertilizer? Agriculture 7, 1.

Ehmann, A., **Bach, I.-M**., Bilbao, J., Lewandowski, I., Müller, T. (2018): Phosphates recycled from semi-liquid manure and digestate are suitable alternative fertilizers for ornamentals. Sci. Hortic. 243, 440-450. (Ehmann & Bach share the first-author ship)

Bach, I.-M.; Essich, L.; Müller, T. (2021): Efficiency of Recycled Biogas Digestates as Phosphorus Fertilizers for Maize. Agriculture, 11, 553.

Bach, I.-M.; Essich, L.; Bauerle, A.; Müller, T. (2022): Efficiency of Phosphorus Fertilizers Derived from Recycled Biogas Digestate as Applied to Maize and Ryegrass in Soils with Different pH. Agriculture, 12(3), 325

Contributions to scientific conferences

Meissner, K., Awiszus, S., Reyer, S., **Bach, I.-M.,** Haag, N., von Cossel, M., Grumaz, C., Frank, D., Müller, J., Müller, T., Öchsner, H., Lewandowski, I., Sohn, K., Egner, S. (2014): GOBI - General Optimization of Biogas Processes. Progress in Biogas III. Stuttgart (GER) (poster presentation)

Bach, I.-M., Idler, L., Müller, T., Lewandowski, I. (2015): Einfluss verschiedener Gärrest-Aufbereitungsprodukte auf die P-Aufnahme bei Mais in einem Löss- und einem tonigen Lehmboden im Vergleich zu einer Mineraldüngung. Deutsche Bodenkundliche Gesellschaft" (DBG), Munich (GER) (oral poster presentation)

Bach, I.-M., Müller, T. (2016): Influence of different recycled digestate fertilizers on P-uptake of maize plants and soil biological processes in different soils. 8th International Phosphorous Workshop (poster IPW 8), Rostock (GER) (oral poster presentation)

Meissner, K., Awiszus, S., Reyer, S., Grumaz, C., **Bach, I.-M**., von Cossel, M., Steinbrenner, J., Müller, T., Oechsner, H., Lewandowski, I., Sohn, K., Müller, J. (2017): General Optimization of Biogas Processes. International „Progress in Biogas Conference" (PIB), Stuttgart (GER) (poster presentation)

Taunusstein, January 2022

12 Declaration

Declaration in lieu of an oath on independent work

according to Sec. 18(3) sentence 5 of the University of Hohenheim’s Doctoral Regulations for the Faculties of Agricultural Sciences, Natural Sciences, and Business, Economics and Social Sciences

1. The dissertation submitted on the topic

Characterization of phosphate fertilizers recycled from biogas digestates and their influence on plant-soil fertility indicators

is work done independently by me.

2. I only used the sources and aids listed and did not make use of any impermissible assistance from third parties. In particular, I marked all content taken word-for-word or paraphrased from other works.

3. I did not use the assistance of a commercial doctoral placement or advising agency.

4. I am aware of the importance of the declaration in lieu of oath and the criminal consequences of false or incomplete declarations in lieu of oath.

I confirm that the declaration above is correct. I declare in lieu of oath that I have declared only the truth to the best of my knowledge and have not omitted anything.

Taunusstein, 07.01.2022

Place, Date Signature

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