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Phosphorus effects of recycled products from municipal wastewater on the soil-plant-system

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

Al_{ox}	Oxalate-soluble Al
BBCH	Biologische Bundesanstalt, Bundessortenamt und chemische Industrie
Ca_{dl}	Double lactate-soluble Ca
CON	Control
DM	Dry matter
DPS	Degree of P saturation
Fe_{ox}	Oxalate-soluble Fe
GLM	General Linear Model
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-OES	Inductively coupled plasma–optical emission spectroscopy
K_{dl}	Double lactate-soluble K
MAP	Magnesium ammonium phosphate ($MgNH_4PO_4$ $6H_2O$) struvite)
Mg_{dl}	Double lactate-soluble Mg
P_{ca}	Citric acid-extractable P
Pconc	P concentration
P_{dl}	Double lactate-soluble P
P_i	Inorganic P
P_o	Organic P
P_{ox}	Oxalate-soluble P
PR	Phosphate rock
PSC	P sorption capacity
P_{tot}, P_t	total P
P_w	Water-soluble P
Res.-P	Residual P
SSA	Sewage sludge ash
SSS	Solar dried sewage sludge
TSP	Triple superphosphate
ut	untreated
XANES	X-ray absorption near edge structure

SUMMARY

Phosphorus (P) is an essential nutrient for food security of a continuously growing world population, but phosphate rock resources are finite. For that reason, recycling of P from waste products becomes increasingly important. Wastewater contains high concentrations of P, but is often loaded with contaminants. Therefore, new processes for recycling P from wastewater streams were developed during the last years. The resulted P recycled products from wastewater need to be evaluated carefully in order to ensure an adequate P supply for crops and to exclude adverse effects on crop growth and the environment. Therefore, in one incubation experiment, two pot experiments and one two-year field experiment the P fertilizing effect of the recycled products were analyzed in comparison to a commercial P fertilizer (triple superphosphate (TSP) and to a control treatment without P application (CON). The used recycled products differed in composition and main P binding form due to the recycling process and raw material used. They included struvite, one solar dried sewage sludge based on Fe-P, one untreated (ut) sewage sludge ash (SSA) based on Al-P (Al(ut)-SSA), one total H_2SO_4-digested SSA based on Al-P (Al-SSA), four thermo-chemically treated SSA combined with subsequent partial H_2SO_4-digestion, which differed in Chloride Donor used (2Mg-SSA: $MgCl_2$, 2Ca-SSA: $CaCl_2$).
In the main pot experiment, the P fertilizing effect of all recycled products on rye, sorghum, amaranth and maize was analyzed, and in the control pot experiment the P effect on maize and sunflower was investigated. In the field experiment only the P fertilizing effect of one recycled product based on Al-P (Al-SSA), Ca-P (1Ca-SSA) and Mg-P (struvite) was analyzed and, in addition to the P effect, the effect of Mg and N contained in struvite on crop yield and P uptake was analyzed in comparison to TSP and CON. In the field experiment in the first year spring barley and in second year forage rye (catch crop) followed by sorghum (main crop) were cultivated. In all experiments, a slightly acidic loamy sand soil was used.

In the incubation experiment, over 70 days the recycled products and TSP increased the bioavailable P immediately after application to the soil, reaching the maximum after 3 days. Whereby the release of bioavailable P by the recycled products increased in the following order: CON < 1Ca-SSA < 2Ca-SSA < Al-SSA = 1Mg-SSA < 2Mg-SSA < TSP < struvite. Struvite increased the readily plant available P the most after one day of incubation, which suggests a high P fertilizer potential for struvite but also a risk of P losses. Among the SSAs, the two Mg-SSAs increased the bioavailable P fractions in soil the most, whereas

lower values were measured after application of the Ca-SSAs and the Al(ut)-SSA due to its high concentration in crystalline P and in case of the Al-SSA as a result of its effect on P sorption capacity in the acidic soil.

The relative P effectiveness (in relation to TSP) of the P products averaged for all cultivated crops in the pot experiments ranged in this order: SSS, Al(ut)-SSA (78%, 84%) < Al- SSA (93%) < both Ca-SSAs (96%)< 1Mg-SSA (99%) < 2Mg-SSA (103%) < struvite (117%). The readily plant available P fractions in the soil increased mainly after the application of struvite, Mg-SSAs and TSP. Among the recycled products, the Al-SSA had the highest effect on the NaOH-P fraction and the Al(ut)-SSA and the Ca-SSA on the H_2SO_4-P fraction. This explained the lower P-bioavailability of the Al-SSA and the Ca-SSA compared to the Mg-SSAs and struvite.

The results of the two-year field experiment showed, that at least in the second year after application the P fertilizing effect of Al-SSA, the Ca-SSA and struvite was in the range of TSP. Whereby, the relative P effectiveness of the recycled products compared to TSP increased in the order Ca-SSA (88 %) ≤ Al-SSA (94%) ≤ struvite (106%). The high effectiveness of P contained in the Al-SSA found in the field experiment for forage rye and sorghum is in contrast to the results of the previous pot experiments, where a lower P uptake in the Al-SSA treatment compared to TSP after cultivation of forage rye and sorghum was found. As described above, the low P availability for crops found in the pot experiment can be related to its effect on P sorption capacity in the first month after addition to acidic soils. However, Al-P contained in soil after the first growing season is thought to be available to plants in the coming growth season. In addition, an Mg fertilizing effect of struvite could be demonstrated.

In summary, these results illustrated that the recycled products studied here are promising renewable P fertilizers, whereby struvite is suited best due to its low contamination level and its high P bioavailability. However, there is still a substantial need for research regarding the P availability of the recycled products under diverse soil conditions (soil pH) and regarding the effect of other ingredients (e.g. contaminants, metals, nutrients) on crop growth. This has to be investigated in long term field experiments to ensure an adequate P supply of these fertilizers under diverse soil conditions and to exclude adverse effects on the soil-plant-system and human health.

ZUSAMMENFASSUNG

Phosphor (P) ist essentiell, um die Ernährungssicherheit einer wachsenden Weltbevölkerung zu gewährleisten; aber die Weltreserven an P sind begrenzt. Aus diesem Grund hat die Rückgewinnung von P aus Reststoffen an Bedeutung gewonnen. Die P-Rückgewinnung aus der Abwasserbehandlung ist aufgrund des hohen P-Rückgewinnungspotentials von hohem Interesse. Aber Abwasser enthält neben P auch Schadstoffe wie Schwermetalle und organische Spurenstoffe. In den letzten Jahren wurden unterschiedliche technische Verfahren entwickelt, um P aus der Abwasserbehandlung zurückzugewinnen. Die daraus resultierenden Recyclingprodukte müssen umfassend untersucht werden, um eine adäquate P-Versorgung der Pflanzen zu gewährleisten und um negative Einflüsse auf die Umwelt und auf den Menschen auszuschließen. Deswegen wurden in einem Inkubationsversuch, zwei Gefäßversuchen und einem Feldversuch die P-Düngewirkung von ausgewählten P-Recyclingprodukten aus der Abwasserbehandlung im Vergleich zu Tripelsuperphosphat (TSP) und einer Kontrolle ohne P-Applikation (CON) untersucht. Diese Recyclingprodukte unterschieden sich in ihrer Zusammensetzung und ihrer P-Verbindung in Abhängigkeit vom eingesetzten P-Fällungsmittel. Bei den untersuchten Recyclingprodukten handelte es sich um Struvit, einen solar getrockneter Klärschlamm (SSS, basierend auf Fe-P), eine unbehandelten (ut) Klärschlammasche (SSA; basierend auf Al-P, Al(ut)-SSA), eine total H_2SO_4-aufgeschlossene SSA (basierend auf Al-P, Al-SSA) und vier thermo-chemisch aufgeschlossene SSAs (basierend auf Mg-P (2 Mg-SSAs) und Ca-P (2 Ca-SSAs). In dem Hauptgefäßversuch wurde der P-Düngeeffekt der Recyclingprodukte auf Mais, Amarant, Hirse sowie auf Grünroggen untersucht und im Kontrollgefäßversuch der auf Mais und Sonnenblume. In dem zweijährigen Feldversuch wurde jeweils der Düngeeffekt von einem Recyclingprodukt untersucht, das auf Al-P (Al-SSA), Ca-P (1Ca-SSA) und Mg-P (Struvit) basierte. In dem zweijährigen Feldversuch wurde im ersten Jahr Sommergerste und im zweiten Jahr Grünroggen als Vorfrucht und Hirse als Zweitfrucht angebaut. Zudem wurde in dem Feldversuch die Wirkung von Struvit auf die Mg- und N-Aufnahme der Pflanzen sowie die Wechselwirkung mit dem Ertrag untersucht. In allen Versuchen wurde ein schwach saurer lehmiger Sand als Boden eingesetzt.

In dem Inkubationsversuch über 70 Tage konnte gezeigt werden, dass die Recyclingprodukte die bioverfügbaren P-Fraktionen direkt nach Applikation erhöhten und ihr Maximum 3 Tage nach Applikation erreichten. Die Freisetzung von bioverfügbarem P

aus den Recyclingprodukten und TSP ist in der folgenden Reihenfolge gestiegen: CON < 1Ca-SSA < 2Ca-SSA < Al-SSA = 1Mg-SSA < 2Mg-SSA < TSP < Struvit. Die hohe Freisetzung von bioverfügbarem P aus Struvit deutet auf eine hohe Pflanzenverfügbarkeit hin, könnte aber auch die Gefahr von P-Verlusten aus der Landwirtschaft steigern. Bei den Klärschlammaschen zeigten die Mg-SSAs die höchste Freisetzung von bioverfügbarem P. Der geringere Effekt der Ca-SSAs und der Al(ut)-SSA auf die bioverfügbaren P-Fraktionen im Vergleich zu den Mg-SSAs lässt sich mit ihren höheren Anteilen an kristallinem P erklären. Der geringere Effekt der Al-SSA auf die bioverfügbaren P Fraktionen beruht auf der Steigerung der P-Sorptionskapazität in dem sauren Boden aufgrund seines hohen Gehalts an amorphen Al.

In den Gefäßversuchen stieg die relative P Effektivität der Recyclingprodukte im Vergleich zu TSP in der Reihenfolge: SSS, Al(ut)-SSA (78%, 84%) < Al- SSA (93%) < beide Ca-SSAs (96%)< 1Mg-SSA (99%) < 2Mg-SSA (103%) < Struvit (117%). Die bioverfügbaren P-Fraktionen wurden am stärksten von Struvit und den Mg-SSAs gesteigert. Demgegegnüber hat die Al-SSA die NaOH-P-Fraktion am stärksten gesteigert und die Al(ut)-SSA sowie die Ca-SSAs hatten den stärksten Effekt auf die H_2SO_4-P-Fraktion. Dieses erklärt auch die geringere P-Effektivität der Al(ut)-SSA, der Al-SSA und der Ca-SSAs im Vergleich zu den Mg-SSAs und Struvit.

Im Feldversuch ist die relative P-Effektivität der Recyclingprodukte im Vergleich zu TSP in folgender Reihenfolge gestiegen: Ca-SSA (88%) ≤ Al-SSA (94%) ≤ Struvit (106%). Der hohe P-Effekt (vergleichbar zu TSP) der Al-SSA auf Roggen und Hirse im zweiten Jahr des Feldversuchs ist im Widerspruch zu den Ergebnissen des Gefäßversuchs, in dem ein geringerer P Effekt der Al-SSA auf Roggen und Sorghum im Vergleich zu TSP festgestellt wurde. Die geringe P-Verfügbarkeit der Al-SSA im Gefäßversuch ist eine Folge des steigernden Effekts der Al-SSA auf die P Sorptionskapazität in den ersten Monaten nach Applikation. Die Ergebnisse aus den Feldversuchen zeigen aber, dass P aus der Al-SSA den Pflanzen in der zweiten Wachstumsphase zur Verfügung steht. Zudem hat Struvit die Mg-Aufnahme, der im zweiten Jahr des Feldversuchs angebauten Fruchtarten, gesteigert.

Zusammenfassend zeigen die Ergebnisse, dass die behandelten SSAs und Struvit sehr effektive erneuerbare P-Dünger sind, wobei Struvit aufgrund seiner sehr geringen Schadstoffbelastung und seiner sehr hohen P-Verfügbarkeit am besten geeignet ist. Aber weiterer Forschungsbedarf ist hinsichtlich der Untersuchung der P-Düngewirkung dieser Recyclingprodukte unter unterschiedlichen Bodenbindungen (u.a. unterschiedlichen pH-

Gehalten) und unter Berücksichtigung weiterer Inhaltsstoffe (z.B. Nährstoffe und Schwermetalle) in Langzeitversuchen erforderlich. Damit eine adequate P-Versorgung der Pflanze gewährleistet werden kann und um negative Effekte auf das Boden-Pflanzen-System auszuschließen.

1 GENERAL INTRODUCTION

1.1 JUSTIFICATION OF THE RESEARCH

The use of animal manure and human excreta as fertilizer have a long history, but were supplemented with guano and later by phosphate rock (PR) due to rapid population growth in the 20th century (Cordell et al., 2009). Currently, mainly PR based fertilizers are used in agriculture, but global PR reserves are limited and most of the PR reserves are located in Morocco (75%) (Jasinski, 2015). The major PR producing countries are China (45%), Morocco (13%) and the USA (11%), whereas in the future the global trade of PR could be completely dependent on Morocco (Jasinski, 2015; Walan et al., 2014). As a consequence of the limited P reserves, the growing world population and the related globally increasing demand of P, the PR cost continue to rise due to investment cost required by new mine capacity (Mew, 2016) and by costs for reduction of contaminants as Cd and uranium. The concentrations of these substances are substantial in new found PR deposits and particularly Cd can be taken up by crops and thus can increase the risk of Cd transfer to the food chain (von Horn and Satorius, 2009; Cordell et al., 2009; Roberts, 2014).

However, the growing application of PR based fertilizers on agricultural land had a positive effect on crop growth, but the increase in P application resulted in high P surpluses in soil. As a consequence, globally 46% of mined P gets lost by surface runoff and erosion, which leads to eutrophication in surface waters (Rittmann et al., 2011; Cordell et al., 2009). The P surpluses are, in addition to PR based fertilizer, mainly associated with manure due to intensification of livestock production (Schoumans et al., 2015). On the other side, other regions are characterized by P deficit due to the limited availability of P fertilizer (Cordell et al., 2009). Therefore, the efficient use of P in agriculture and P recycling from waste products for food production are the primary concern (Elser et al, 2014). The P cycle can only be closed by recycling P from wastewater and animal manure and by the transfer of P from regions with P surplus to regions with P deficit (Schoumans et al., 2015).

Animal manure (40% of mined PR) and wastewater (16% of mined PR) are important sources to recover P as both contain high P concentrations of the input of mined PR (Rittmann et al., 2011; Cordell et al., 2009). In Europe 45% to 55% (Eastern Europe) of P input are provided by manure, but as described above in intensive livestock regions the use of animal manure led to P surpluses in agriculture (Schoumans et al., 2015). Currently, P recycling from manure is not viable due to the decentralized structure of animal production and the associated transport cost (Sharpley et al., 2015; Schoumans et al., 2015). Therefore, a more balanced and less intensive system of livestock production is an option to facilitate manure P application at rates that are aligned with crop needs.

Municipal wastewater is a viable source for recovering P in larger quantities, due to its more centralized structure (Sharpley et al., 2015). In Europe, P from municipal wastewater is predominantly recovered and reused in agriculture in form of sewage sludge (a byproduct of wastewater treatment) (Cordell et al., 2011; Schoumans et al., 2015). However, sewage sludge is often rich in heavy metals and organic contaminants. Therefore, the direct application of sewage sludge is increasingly questioned and some European member states already restricted (e.g. Germany) or banned (e.g. Switzerland) the direct application of sewage sludge (Kabbe et al., 2015; Hukari et al., 2016). Consequently, in recent years several new processes were developed to recover P from wastewater stream or residues from wastewater treatment. The resulting recycled products from wastewater treatment need to be investigated carefully to ensure an adequate P supply for crops and to exclude adverse effects on the environment and human health.

1.2 RECYCLED PRODUCTS FROM MUNICIPAL WASTEWATER TREATMENT IN GERMANY

In Germany, the P potential of municipal wastewater is about 75,000 t annually. Sewage sludge contains about 60,000 t P annually, whereby approximately 24% of sewage sludge is used directly as fertilizer in agriculture and 64% of sewage sludge is incinerated (Figure 1-1) (BMUB, 2016; Montag et al., 2015). However, the direct use of sewage sludge as fertilizer is declining in Germany due to its high concentration in harmful substances (BMU, 2015). From 2012 to 2015, the use of sewage sludge in agriculture decreased (29% to 24%), while the incineration of sewage sludge increased (55% to 64%) (Destatis, 2015). This trend is likely to continue over the next few years due to the restriction of sewage sludge application and the stricter limits for contaminants established by law. Consequently, several new processes are currently being developed to regain P from the wastewater treatment.

There are two main paths to recycle P from wastewater treatment: (1) P precipitation from digested sludge or from process water as struvite and (2) technical recycling from ashes of mono incinerated sewage sludge (sewage sludge ash, SSA) (Kabbe et al., 2015; Montag et al., 2015). Only 5% of the SSAs are used as fertilizer and struvite is used far more sparingly in agriculture than SSAs (Krüger and Adam, 2015). In the following these recycling processes are described in more detail

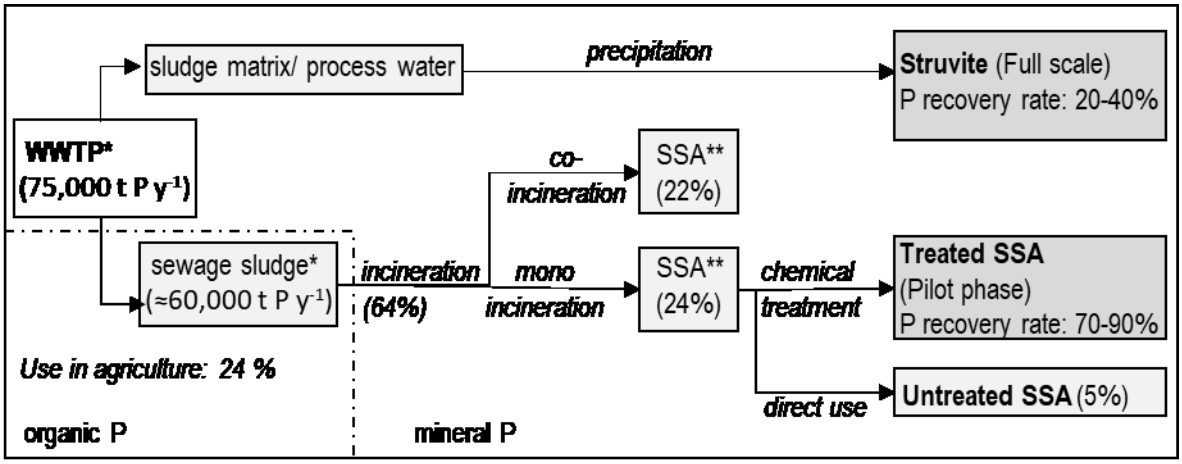

Figure 1-1 P cycle, showing major inputs, outputs and soil processes. * BMUB, 2016; Montag et al., 2015, ** Krüger and Adam, 2015

Struvite can be recovered prior to the dewatering in the sludge matrix or from the process water after dewatering (Egle et al., 2015). The struvite recovered within the sludge matrix can include more impurities than struvite recovered from the process water, but both struvite products are within the limits set by the German fertilizer ordinance (DüMV) and some struvite-products (e.g. Berliner Pflanze (AirPrex)) are already officially certified as safe fertilizer in Germany (Kabbe et al., 2015; Egle et al., 2015). Both processes for struvite precipitating are already implemented and operating in full scale (Table 1-1) (Kabbe et al., 2015; Montag et al. 2015). But the operational benefits of struvite recovered within the sludge matrix are higher compared to struvite recovered from the process water and is consequently profitable regardless of the sale price due to the increased efficiency of the sludge dewatering and the lower maintenance cost (reduction of clocking and abrasion) (Kabbe et al., 2015; Montag et al., 2015; Egle et al., 2015). However, it must be considered, that P recovery by struvite precipitation is limited to wastewater treatment plants with enhanced biological P removal, which applies to 6% of the wastewater treatment plants in Germany (related to population equivalents) (Montag et al., 2015). According to the respective P recovery potential, 5% to 45 % of the P in wastewater inlet can be recovered using struvite precipitation (Montag et al., 2015; Kabbe et al., 2015).

Sewage sludge needs to be mono incinerated if its P concentration is ≥ 20 g kg DM^{-1} to ensure a high P concentration in the resulting SSA (Kraus et al., 2016). During incineration, organic contaminants get destroyed, but SSA contains high amounts of heavy metals and thus mostly has to be treated to achieve the limit values established by law (Krüger and Adam, 2015; Nancer et al., 2014b). In addition, further treatment of the raw SSA is generally required to increase its P availability for crops (Krüger and Adam, 2015; Nancer et al., 2014b). The processes for recovering P from mono incinerated SSA include wet-chemical and thermo-chemical processes, which are currently tested in lab or demo phase (Table 1-1). The P recovery potential of treated SSA is very high with up to 90% of the P in wastewater inlet (Figure 1-1) (Montag et al., 2015; Kabbe et al., 2015; Krüger and Adam, 2015), but the whole P recovery process (including the mono incineration and the post treatment) of the SSA is a cost intensive process (Montag et al., 2015; Kabbe et al., 2015; Krüger and Adam, 2015). In addition, the modules for the thermal treatment should be integrated in the mono incineration facilities to achieve energy savings (Hermann, 2013).

Table 1-1 German processes and technologies for P recovery from wastewater and their state of maturity (operation) as well as resulting end product (Source: Kabbe et al., 2015; Montag et al., 2015).

	Process	Technology	Operation	Product
Liquor[1]	- Precipitation	- P-RoC - RePhos	- Demo scale - Full scale	- Ca-P - struvite
Sludge[2]	- Precipitation	- FixPhos - AirPrex - Lysogest	- Full scale - Full scale - Full scale	- Ca-P - struvite - struvite
	- Enforced P dissolution	- Stuttgarter-process - Budenheim-process - Gifhorn-process	- Demo scale - Demo scale - Full scale	- struvite - Ca-P - struvite
SSA[3]	- Thermal	- AshDec/Outotec - RecoPhos - Mephrec	- Demo scale - Lab scale - Demo scale	- P-mineral - H_3PO_4/ P_4 - P-slag
	- Acidic digestion	- Fertilizer Industrie - SESAL-Phos	- Demo scale - Lab scale	- Mineral fertilizer - Ca-P

1= Process water, 2= Digested sludge 3= Sewage sludge ash.

However, the quality of the recycled products is, in addition to the P recovery rate and the economic feasibility, mainly related to their P bioavailability and their effects on soil-plant -system in order to ensure an adequate P supply for crops and to avoid adverse effects on the environment and human health.

Therefore, in this study, the P fertilizer quality of 6 mono incinerated SSAs and struvite (AirPrex) compared to a commercial rock phosphate based fertilizer, triple superphosphate (TSP) and a solar dried sewage sludge based on Fe-P (SSS), were analyzed. The SSAs differed in treatment and consequently in their composition: one untreated (ut) SSA based on Al-P (Al(ut)-SSA), one wet-chemical treated SSA based on Al-P (Al-SSA, precursor product of SESAL) and four thermo-chemical treated SSAs (AshDec/Outotec) by two based on Mg-P and two on Ca-P (Mg-SSA, Ca-SSA) in respect of used Chlorine Donor during treatment. Consequently, the here studied recycled products from wastewater differed in the used P precipitating agent, which enable to determine the effect of the P precipitating agent on P speciation and on P bioavailability of the recycled products.

1.3 Status and development of P recycled products from wastewater in Germany

According to Germany's current coalition agreement (as of November 27, 2013) the direct application of sewage sludge on agricultural land is to be ended and the recovery of P and other nutrients from wastewater treatment plants is to be undertaken in order to avoid the accumulation of organic contaminants in the soil (BMU, 2015; Kabbe et al., 2015).

Table 1-2 Limit values for heavy metals and organic contaminants of the German Sewage Sludge Ordinance (AbfKlärV) and the German Fertilizer Ordinance (DüMV) in its current version and the planned version of the AbfKlärV.

	AbfKlärV (1992)	**DüMV (2012)**	**AbfKlärV (new version)**
As (mg kg^{-1} DM^{-1})	-	40	DüMV
Pb (mg kg^{-1} DM^{-1})	900	150	DüMV
Cd (mg kg^{-1} DM^{-1})	10	1.5 (50)*	DüMV
Cr (mg kg^{-1} DM^{-1})	900	-	DüMV
Cr^{IV} (mg kg^{-1} DM^{-1})	-	2	DüMV
Cu (mg kg^{-1} DM^{-1})	800	900	DüMV
Ni (mg kg^{-1} DM^{-1})	200	80	DüMV
Hg (mg kg^{-1} DM^{-1})	8	1	DüMV
Zn (mg kg^{-1} DM^{-1})	2.500	5.000	4.000
Tl (mg kg^{-1} DM^{-1})	-	1	-
AOX1) (mg kg^{-1} DM^{-1})	500	-	400
B(a)P2) (mg kg^{-1} DM^{-1})	-	-	1
PCB3) (mg kg^{-1} DM^{-1})	0.2	-	0.1
PCDD/F4) (ng kg^{-1} DM^{-1})	100	-	-
PFT5) (mg kg^{-1} DM^{-1})	-	-	-
I-TE Dioxie und dl-PCB6) (ng kg^{-1} DM^{-1})	-	30	DüMV

DM dry matter *value for fertilizer > 5 % P_2O_5 of dry matter yield (DM). 1) adsorbable organic halogens. 2) benzo[a]pyrene. 3) polychlorinated biphenyls; limit values for each of congeners No. 28, 52, 101, 138, 153,180. 4) polychlorinated dibenzodioxins and furans. 5) sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS). 6) sum of dioxins and dioxin-like polychlorinated biphenyls (dl-PCB)

In Germany, the use of P recovered from municipal wastewater in agriculture was regulated by the Sewage Sludge Ordinance (AbfKlärV) of April 1992. Since January 2015 the more lenient limits of the AbfKlärV have been replaced by the stricter limits of the DüMV (BMU, 2015) and in January 2017 the German cabinet approved a draft of the sewage sludge ordinance. However, the new sewage sludge ordinance may come into force by 1st January 2018. The new version of the AbfKlärV will regulate the restriction of direct sewage sludge application on soil to promote recovering of P from wastewater treatment and to reduce the level of contaminants (BMU, 2015). According to the new AbfKlärV, the direct application of sewage sludge from smaller wastewater treatment plants (capacity in relation to population equivalent < 50,000) on agricultural land is still permitted, but the limits of the DüMV will be supplemented by further limits set in the planned AbfklärV (Table 1-2) and more regular quality assurance checks will be carried out (BMU, 2015; BMU, 2017). This ensures a low contamination level of sewage sludge from smaller wastewater treatment plants in Germany. In contrast, P needs to be recovered from sewage sludge of larger wastewater treatment plants after a certain transition period (Kraus et al., 2016; BMU, 2015). The transition period is related to the size of the wastewater treatment plant and is 12 years for plants with a population equivalent > 100,000 and 15 years for plants with a population equivalent > 50,000 (Kraus et al., 2016; BMU, 2015).

In Germany a total of 9,988 billion m^3 of wastewater was treated in municipal wastewater treatment plants and 1,8 million tons of sewage sludge were produced in 2010 (DWA, 2014). According to the DWA 2014 about 61% of total treated wastewater volume was obtained from larger wastewater treatment plants (> 50,000 population equivalent) (Table 1-3).

Table 1-3 Number of wastewater treatment plants (WWTP) by size and proportion of total treated wastewater volume (Proportion of WWt) in Germany (DWA, 2014).

Number of WWTP	**Size** Population equivalent	**Proportion of WWt** %
9061	< 50,000	38,9
315	< 100,000	13,8
256	> 100,000	47,3

There are twenty-six facilities for mono incineration of sewage sludge in Germany, where 800.000 t of sewage sludge are used as fuel and 300.000 t of SSA are produced. Consequently, the technical facilities required for the mono incineration need to be established first (capacity for mono incineration needs to be increased by 70%) as the whole amount of sewage sludge from the larger wastewater treatment plants (capacity in relation to population equivalent > 100,000) will be mono incinerated in Germany (Montag et al., 2015).

1.4 EVALUATION OF THE FERTILIZER QUALITY OF RECYCLED PRODUCTS FROM WASTEWATER TREATMENT

1.4.1 P speciation

Several authors showed that P solubility of recycled products from wastewater treatment is strongly influenced by P speciation and composition (Römer, 2006; Vogel et al., 2013; Nancer et al., 2014a), which highlights the importance to comprehensively evaluate the quality and performance of such alternative P fertilizers and fertilizer production processes. There are several methods available to characterize the P composition in soils and fertilizers. The sequential P extraction is a common wet chemical method, which differentiates between labile P, Al- and Fe- associated P and Ca associated P (Hedley et al., 1982). However, the sequential extraction does not necessarily allow conclusions on P speciation. In contrast, the P K-edge X-ray absorption near edge structure (XANES) spectroscopy is capable of delivering element-specific and non-invasive direct speciation of P in the solid phase (Kruse et al., 2015), which has been successfully used to determine track P speciation in various P fertilizer treatments including SSAs (e.g. Ajiboye et al., 2008; Siebers et al., 2013; Nancer et al., 2014a). Therefore, a combination of sequential P extraction with XANES is of unique importance to gain substantial information about the P species of the recycled products, which contributes to better understand their P dissolution behavior in soil and consequently their P availability for plants.

The composition of struvite precipitated during wastewater treatment is close to the theoretical composition of pure struvite (Degryse et al., 2016). The P speciation and thus the P solubility of SSA depend on the composition of the raw SSA and used recycling process (Donatello and Cheeseman, 2013). Thereby, the P speciation in the raw SSA is mainly affected by the agents used for P precipitation during wastewater treatment, which are mainly $FeCl_3$ or $Al_2(SO_4)_3$. (Donatello and Cheeseman, 2013). Raw SSA contains high amounts of crystalline P (e.g. quartz, whitlockite, hematite and feldspar) (Nancer et al., 2014a; Donatello and Cheeseman, 2013). Crystalline P (primary P minerals) is only of minor significance to provide P for crop production due to their sparingly solubility (Akhtar et al., 2009). For that reason, raw SSAs are mostly treated to increase the P bioavailability (Donatello and Cheesman, 2013). The P fractions in treated SSAs vary considerably according to the used precipitating agent during the whole P recycling process and include readily soluble P and P adsorbed and precipitated on Al-, Fe-, Mg- and Ca-compounds (Nancer et al., 2014; Donatello and Cheesman, 2013; Rahman et al., 2014).

1.4.2 Dissolution kinetics

For the profound understanding of the bioavailability of P contained in the recycled products first the dissolution of P from such substrates in soil needs to be understood. Plants absorb P in the form of orthophosphate ($H_2PO_4^-$, HPO_4^{2-}) from the soil solution, which occurs in soil in very low concentrations only (Vance et al., 2003; Blume et al., 2016).

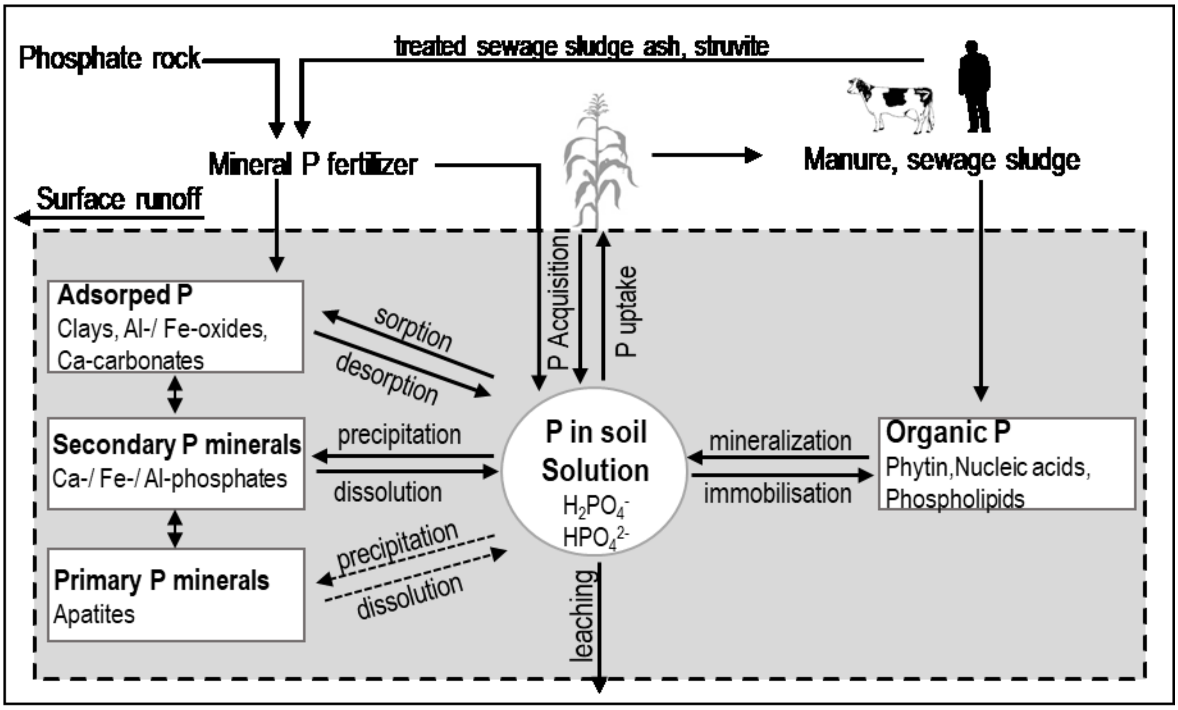

Figure 1-2 P cycle, showing major inputs (referred to chapter 1.1), outputs and soil processes.

The readily soluble P added to the soil by the recycled products can be adsorbed, precipitated or transformed into organic P. On the other side, adsorbed and precipitated P of the recycled products and of soil P can be desorbed, dissolved or mineralized to become available for plants (Figure 1-2) (McDowell et al., 2001). The P concentration in soil solution is strongly influenced by the soil pH and the concentration of metals (Mg, Ca, Al, Fe) (Lindsay, 1979; Sanyal and DeDatta, 1991; Hinsinger, 2001), which can be enriched by the recycled products as metals are present in widely varying amounts in the recycled products (Petzet et al., 2012; Krüger and Adam, 2015; Donatello and Cheesman, 2013; Rahman et al., 2014). Whereby, in acidic soil P is adsorbed or precipitated mainly on Al and Fe and mainly on Ca and Mg under alkaline soil conditions (McDowell et al., 2001; Matar et al., 1992; Comerford, 1998). However, there is only little information about the P reaction mechanism in soil of the herewith studied recycled products from wastewater. In particular, the mechanisms of struvite dissolution in soil are still unclear (Talboys et al., 2016). This highlights the importance to determine the dissolution behavior of the studied recycled products here in an incubation experiment.

1.4.3 P bioavailability of the recycled products from wastewater

The P fertilizing effect of the recycled products of wastewater treatment is also influenced by the cultivated crop due to differences in their P use efficiency. Plants have different adaptation mechanisms to improve the P acquisition in case of P deficiency (Table 1-4) (Vance et al., 2003; Ramaekers et al., 2010; Richardson et al., 2011). Differences of the P use efficiency were observed between C_3-plants and C_4-plants (Sage and McKown, 2006; Ghannoum, 2009; Plaxton and Lambers, 2015) and between monocots and dicots (Ramaekers et al., 2010; Rich and Watt, 2012; Niu et al., 2013).

Table 1-4 Mechanism of Phosphorus efficiency in plants (Ramaekers et al., 2010)

Strategy	Adaptations
P uptake efficiency	- Altered root morphology and architecture - Increased root hair density and length - Plant-microbial associations - Arbuscular mycorrhizal symbioses - Root Exudation (e.g. organic acids, phosphatases, protons)
P utilization efficiency	- Increased growth per unit of P uptake - Increased Efficiency of cellular P uptake - Modification of carbon metabolism and membrane structure - Alternative Respiratory pathways

For instance, the C_4-photosynthesis has a higher photosynthetic P use efficiency than the C_3-photosynthesis (Ghannoum, 2009), while C_4-plants react more sensitive to P deficiency (Sage and McKown, 2006). In contrast, Halsted and Lynch (1996) observed no differences in P use efficiency of C_3-grasses compared to C_4-grasses, but a higher P use efficiency of monocots compared to dicots. Talboys et al. (2016) observed in a pot experiment with buckwheat (dicot) and spring wheat (monocot), that the P fertilizing effect of struvite was increased by the higher organic acid exudation of buckwheat compared to spring wheat. The P bioavailability of struvite and SSAs for different crops compared to commercial rock phosphate based fertilizer were analyzed in various pot experiments. According to these pot experiments struvite is as effective as commercial P fertilizers for several crops (e.g. maize, ryegrass, buck wheat, spring wheat) under acidic to slightly alkaline soil conditions (e.g. Talboys et al., 2016; Severin et al., 2013; Johnston and Richards, 2003). The P fertilizing effectiveness of treated SSA is ≥ 80% compared to TSP for crops (e.g. maize, rye grass) and thus also a valuable P fertilizer (Römer, 2006; Severin et al., 2013; Wilken et al., 2015). However, differences of the P fertilizing effect of these recycled products on monocots and dicots as well as on C_3-species and C_4-species have not been thoroughly examined yet. As mentioned above, in all these studies the P bioavailability of the recycled products from wastewater were analyzed in pot experiments, while information about the P fertilizing effects of the recycled products in the field is rare. Pot experiments are necessary to produce replicable and comparable data, but pot conditions are very different from field conditions (e.g. soil temperature, aeration, water content) (Passioura, 2006). Consequently, results obtained in pot experiments often differ largely from results obtained in the field. This illustrates the importance to evaluate the P fertilizing effect of recycled products from wastewater in both, pot and field experiments in order to obtain reasonably valid results.

1.5 GENERAL AND SPECIFIC OBJECTIVES

Against the background of lacking P deposits in Germany, P recycling from wastewater is of great importance. The general objectives of this work were to investigate the P fertilizer quality of the recycled products from wastewater treatment comprehensively in order to assess the future significance of these recycled products to replace PR based fertilizers.

The specific objectives include:

- Determining the nutrient and heavy metal composition and particularly the chemical P solubility and P-speciation of the recycled products to evaluate their potential P fertilizing efficiency and the potential risk of soil contamination from residual heavy metals in these products.
- Investigating the P release kinetics of the recycled products in dependency of soil parameters of a moderate acidic loamy sand.
- Analyzing the P availability of the recycled products for different common crops in pot experiments and to determine the effect of monocots and dicots as well as of C_3-species and C_4-species on the P bioavailability of the studied recycled products here.
- Evaluating the effect of the recycled products on the P cycle in soil after cultivation of different crops.
- Estimating the effect of the recycled products under natural conditions on dry matter yield and P uptake of different crops and the effect of N and Mg contained in struvite on P uptake and yield of the cultivated crops in one field experiment.

1.6 STRUCTURE OF THE THESIS

The fertilizer quality of the recycled products from wastewater treatment is analyzed comprehensively from the chemical P availability in the laboratory to the P availability for plants in the field (Figure 1-3).

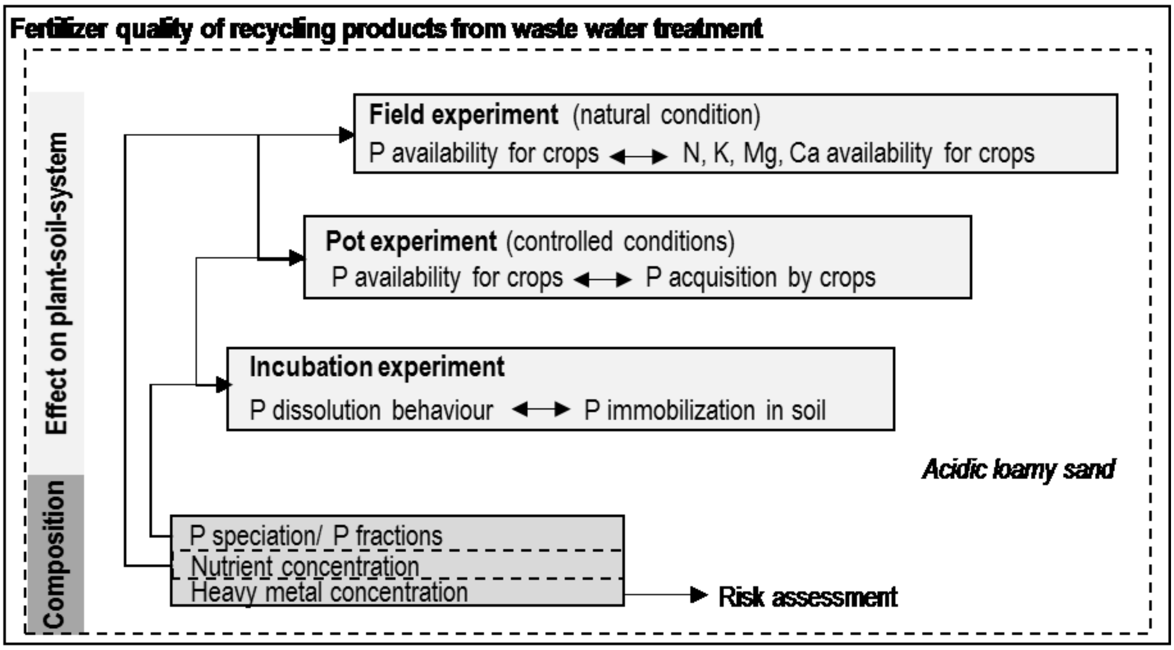

Figure 1-3 Structure of the thesis

In the second chapter the composition, chemical P solubility and P speciation of the recycled products and their dissolution behavior in soil were analyzed. In addition, the risks of heavy metal accumulation in soil and of heavy metal uptake by crops were estimated on the basis of the heavy metal concentration of the recycled products. These findings form the basis for understanding the P bioavailability of the recycled products, which were analyzed in two pot experiments and one two-year field experiment.

Table 1-5 Cultivated crops in the pot experiments

	C_3-plants	C_4-plants
Monocots	forage rye (*Secale cerealeL.)*	maize (*Zea mays L.)* sorghum (*Sorghum bicolor* (L.) Moench)
Dicots	Sunflower (*Helianthus annuus L.)*	amaranth (*Amaranthus L.)*

In the third chapter the P availability of the recycled products for different crops and their effect on P cycle in soil was investigated in two pot experiments under semi controlled conditions outside in cages. In the pot experiments the fertilizing effect of the recycled products on different crops including monocots and dicots of C_3-species and C_4-species was analyzed to determine their effect on the P bioavailability of the studied recycled products (Table 1-5).

In the pot experiments a further P treatment, a solar dried sewage sludge based on Fe-P, was implemented to determine the effect of the P recycling processes on the P bioavailability of the recycled products. The focus of the thesis lies on the main pot experiment as indicated by the high scope of investigations (Table 1-6). The results of the main pot experiment were confirmed by a second smaller control pot experiment.

Table 1-6 Scope of investigations

Experiment	Soil	Plant	
Field experiment 2010: spring barley 2011: forage rye – sorghum	• Labile P pools • pH	• P-uptake • N- and Mg-uptake • Yield	**Plant - Soil - System**
Control pot experiment Maize Sunflower	• Labile P pools • pH	• P-uptake • Yield	
Main pot experiment Maize Amaranth Forage rye Sorghum	• P fractions (Hedley) • pH	• P-uptake • Yield • P acquisition by crops	
Composition/ Incubation experiment P speciation (XANES) P solubility Nutrients Heavy Metals	• Labile P fractions • P sorption capacity • pH		**Basis**

In the final step (chapter 4), the P fertilizing effect of the recycled products on different common crops was studied in the field in order to analyze their suitability as P fertilizer under natural conditions. In addition, in these field experiments the effect of N and Mg contained in struvite on crop yield and P uptake were analyzed compared to CON and TSP. In all experiments, an acidic soil was used since acidic soils are commonly associated with P deficiency and approximately 50% of global arable land is acidic (von Uexküll and Mutert, 1995).

All chapters are highly interlinked with each other and thus the results of all experiments were compared in chapter 5 and discussed in the context of the current technical and legal conditions in Germany.

2 RECYCLED PRODUCTS FROM MUNICIPAL WASTEWATER: COMPOSITION AND EFFECTS ON PHOSPHORUS MOBILITY IN A SANDY SOIL

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2.1 ABSTRACT

Recycled products from wastewater may contain high concentrations of phosphorus (P) and are thus promising alternative fertilizers. However, to better predict their P fertilizer efficiency and potential for P leaching, investigations on P forms and P mobility in soil are essential. In this study, different recycled products - an untreated sewage sludge ash (SSA), a H_2SO_4-digested SSA, four thermo-chemically treated SSAs (two Mg-SSAs and two Ca-SSAs), and struvite -were investigated using a combination of wet chemical methods and P K-edge X-ray absorption near-edge structure (XANES) spectroscopy concerning their composition and their effects on P sorption in a sandy soil in comparison with triple superphosphate.

Most of the P in the SSAs was associated with Ca in stable P fractions. The lowest P values in labile fractions (H_2O-P, $NaHCO_3$-P) were found for the untreated SSA and struvite. However, the addition of struvite resulted in an immediate increase in the bioavailable P fractions and the degree of P saturation in soil after only 1 d of incubation. This suggests a

high P fertilizer potential for struvite but also a risk of P losses. Among the SSAs, the two Mg-SSAs increased the bioavailable P fractions in soil the most, whereas lowest values were measured after application of the untreated SSA. Our results demonstrate that chemical analyses of recycled P products may involve the risk of misjudging the fertilizer quality when carried out alone, without considering the behavior of these products in soil.

2.2 INTRODUCTION

Phosphorus (P) is an essential crop nutrient, making it indispensable in maintaining food security for a continuously growing world population. Most mined phosphate rock (PR) is used in agriculture, although up to 46% of the P it supplies is lost globally through agricultural runoff and erosion. Considerable uncertainties exist about the extent of the remaining phosphate rock reserves, projected to last for 40 to 400 years (e.g., Cordell et al., 2009; Elser, 2012; Jasinski, 2014). Therefore, it is essential to establish a more sustainable management of the P mass flow, moving toward global use of P that is both sufficient and efficient. In this context, the recovery and recycling of P offers great potential, and several secondary phosphate resources of plant and animal origin have already been shown to be valuable P sources for plant production (Vassilev et al., 2013, Bachmann et al., 2014).

Residuals from wastewater treatment (e.g., sewage sludge) pose significant potential for P recovery, with about 3 MT P each year globally (Elser, 2012). At one time, sewage sludge was directly applied to agricultural soils (e.g., Singh and Agrawal, 2007; Nanzer et al., 2014b), but this practice has disappeared in many countries because untreated sewage sludge poses the risk of releasing potentially toxic substances (e.g., Renner, 2000). Therefore, several technologies have been developed to recycle P from wastewater (Sartorius et al., 2012). Two of the most promising P-recovery processes are the mono incineration of sewage sludge combined with chemical treatment of the resulting sewage sludge ashes (SSA), and the precipitation of P as magnesium-ammonium-phosphate ($MgNH_4PO_4$ $6H_2O$, struvite) from digested sludge (Sartorius et al, 2012; Vogel et al., 2015). These wastewater products may differ in P composition, depending on the raw material used and the treatments applied (Römer, 2006; Vogel et al., 2013; Nanzer et al., 2014a), which subsequently affects P solubility and agronomic efficiency.

Several methods are available to characterize P composition in materials and soils. Sequential P extraction is a common wet chemical method to obtain P fractions based on different solubility (Hedley et al., 1982). This method yields operationally defined P fractions, which do not necessarily allow conclusions regarding P speciation. Therefore, wet chemical methods should be combined with complementary methods such as P K-edge X-ray absorption near edge structure (XANES) spectroscopy, capable of delivering element-specific and non-invasive direct speciation of P in the solid phase (Kruse et al., 2015). P K-edge XANES spectroscopy has also been used to track P speciation in soil in various P fertilizer treatments (e.g., Toor et al., 2005; Ajiboye et al., 2008, Siebers et al., 2013).

In addition to nutrient content and agronomic efficiency of recycled products, their behavior in the environment, particularly their contribution to nutrient losses from agricultural land, is also of interest. The solubility and transport of P compounds in soil are affected not only by P speciation and composition of the fertilizers, but also by soil characteristics such as the P sorption capacity and the degree of P saturation (Hansen et al., 2002). The P sorption capacity in soil depends on clay content; clay mineralogy; organic matter content; concentrations of exchangeable aluminum (Al), iron (Fe), and calcium (Ca), and pH (Schoumans, 2000). The investigation of the dissolution behavior of wastewater products, as well as their effects on the P sorption capacity, has been considered particularly important for sandy soils because of their low clay and silt content and the resulting higher risk of P losses (Blume et al., 2010). In neutral to acidic soils P is mainly adsorbed to Al- and Fe-oxide, and the sum of the oxalate soluble Al (Al_{ox}) and Fe (Fe_{ox}) contents is fairly well correlated with the Freundlich coefficient (Gustafson et al., 2012). Several authors observed that Al- and Fe-rich sewage sludge products can increase the sorption capacity in soil (Dayton and Basta, 2005; Krogstadt et al., 2005; Bøen et al., 2013) and therefore may reduce the risk of P losses. On the other hand, a strong fixation of P to Al- and Fe-oxides/hydroxides can decrease the bioavailability of P, with negative impacts on plant nutrition. Incubation studies are a suitable tool to get robust information on plant P availability and risks of P losses (Nanzer et al., 2014b) and thus can contribute to optimizing fertilizer management with recycled products.

The objectives of this study were to comprehensively characterize recycled wastewater products with respect to (i) elemental composition, (ii) P fractions and chemical P forms, and (iii) P release in an incubation experiment, to better predict their fertilizing value and their potential for P leaching. We included five differently treated SSAs, one untreated SSA, and struvite as recycled products in this study and compared them with a highly soluble commercial P fertilizer, triple superphosphate (TSP).

2.3 MATERIALS AND METHODS

2.3.1 Fertilizer and soil characteristics and experimental design

Six sewage sludge ashes (SSAs, with nomenclature chosen according to the treatments applied) and struvite were investigated regarding their composition and their effects on P sorption in a sandy soil in comparison with TSP. The same recycled products were used in a previous experiment carried out by Vogel et al. (2015). For the untreated (ut) ash, sewage sludge was mono incinerated after P had been precipitated from the wastewater using aluminum (Al) salt (Al(ut)-SSA). The five treated SSAs were also derived from mono incinerated sludge and were treated to increase the solubility of P and reduce the concentration of heavy metals. For Al-SSA, P was also precipitated with Al before the sludge was mono incinerated. The ash was then treated by full H_2SO_4 digestion. The other four SSAs (1Mg-SSA, 2Mg-SSA, 1Ca-SSA, and 2Ca-SSA) were thermo-chemically treated, whereby heavy metals were evaporated in a rotary furnace at a temperature of about ≈1000°C after adding $MgCl_2$ (Mg-SSAs) or $CaCl_2$ (Ca-SSAs) as a chlorine donor at a rate of 100 mg kg^{-1} ash. A more detailed description of the process can be found in Mattenberger et al. (2008) and Adam et al. (2009). Following this, 30% H_2SO_4 (v/v) was added to increase the P availability. The raw sewage sludge used to produce the two Mg-SSAs and Ca-SSAs came from different batches of the same wastewater treatment plant. The struvite (magnesium ammonium phosphate) was produced according to a process developed by Berliner Wasserbetriebe (BWB), in which the digested sludge is aerated in a reactor to raise the pH to 8 for struvite precipitation by stripping CO_2 and adding $MgCl_2$ (Kern et al., 2008). Highly soluble TSP was used as a mineral fertilizer reference because this is one of the most commonly used P fertilizers. The products were analyzed in three replicates for nutrients, heavy metals, and P fractions (Figure 2-1, Table 2-1).

The soil used for the incubation experiment was a moderately acidic loamy sand (pH 5.2), classified according to the World Reference Base for Soil Resources as a Stagnic Cambisol. The soil was collected from the A horizon of a field experiment carried out at the experimental station of the University of Rostock (see also Requejo and Eichler-Löbermann, 2014). The plant-available P concentration measured as double-lactate-soluble P (P_{dl}) was 50 mg kg^{-1} soil, indicating a suboptimal P supply (Schweder and Kape, 2004). The total P concentration (P_{tot}) of the soil was 515 mg kg^{-1}, the Ca_t concentration was 1745 mg kg^{-1}, the organic matter was 2.31%, and the degree of P saturation (DPS) in the soil was 45%.

Table 2-1 Concentrations of total P (Ptot), citric acid soluble P (Pca), sequentially extracted inorganic P fractions (Pi) and residual P (Res.-P) of the recycled products and triple superphosphate (TSP).

	P_{tot}	P_{ca}	H_2O- P_i	$NaHCO_3$- P_i	NaOH- P_i	H_2SO_4- P_i	Res.- P
	g kg^{-1}						
Al-(ut)SSA	98.6	29.9 ± 9.6	0.1 ± 0.0	0.3 ± 0.0	23.4 ± 0.6	74.1 ± 12.0	0.7
Al-SSA	58.5	47.1 ± 1.7	21.6 ± 2.3	3.7 ± 0.0	19.9 ± 0.9	0.9 ± 0.4	12.4
1Ca-SSA	44.4	29.1 ± 6.2	4.7 ± 0.1	2.5 ± 0.0	8.0 ± 0.5	17.7 ± 1.6	11.5
2Ca-SSA	62.4	46.0 ± 0.3	16.1 ± 0.3	2.7 ± 0.1	6.3 ± 1.2	24.5 ± 1.8	12.8
1Mg-SSA	39.4	30.5 ± 7.1	9.8 ± 0.3	2.2 ± 0.0	11.3 ± 0.2	14.3 ± 1.5	1.8
2Mg-SSA	65.9	53.6 ± 6.5	26.7 ± 0.7	3.8 ± 0.1	3.6 ± 0.3	13.9 ± 0.9	17.9
Struvite	121.7	102.7 ± 3.8	3.7 ± 0.2	7.8 ± 0.0	16.7 ± 0.7	67.3 ± 13.4	26.2
TSP	178.2	177.8 ± 6.4	148.3 ± 1.1	0.6 ± 0.0	2.7 ± 0.8	9.5 ± 0.5	17.1

SSA= sewage sludge ash, ut= untreated, Res.= Residual

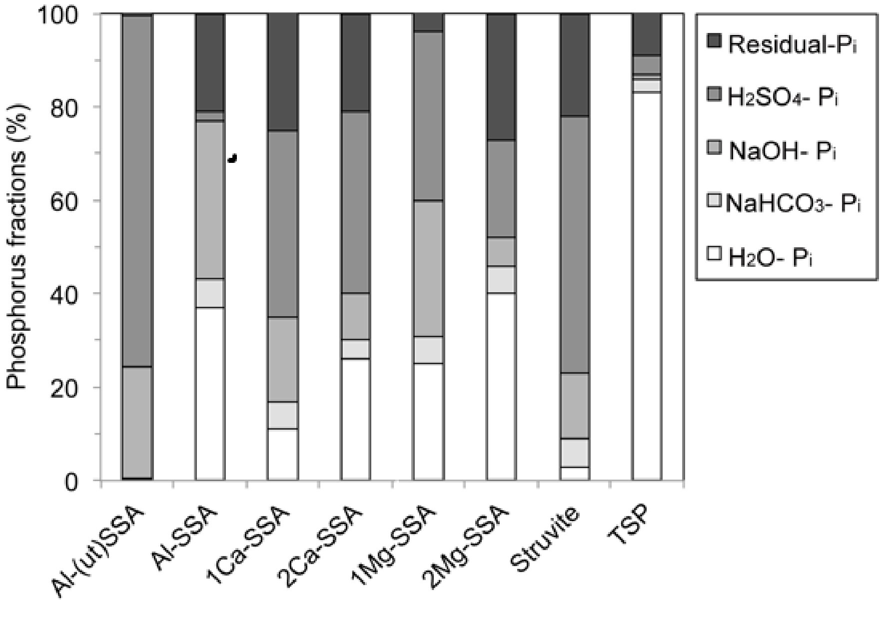

Figure 2-1 Proportions (% of the total P) of sequentially inorganic extracted P fractions (Pi) of the recycled products and triple superphosphate (TSP). SSA= sewage sludge ash, ut= untreated

For incubation, 100 g of the air-dried and sieved soil was spiked with the recycled products and the TSP fertilizer in order to increase the initial total P (P_{tot}) level of the soil by 400 mg P kg^{-1} soil. A control without P addition was also established. Deionized water was added daily to maintain water content at 60 to 70% of the water-holding capacity by weight. The treatments were incubated at 20°C in the dark in 100-mL polyethylene containers. Each container was covered with a plastic paraffin film with ventilation holes to minimize moisture loss while allowing air exchange during incubation. Each treatment consisted of three replicates. Subsamples were taken at intervals of 1, 3, 7, 14, 35, and 70 days of incubation

2.3.2 Analytical procedure

The recycled products and TSP were analyzed for total nutrient and heavy metal concentration using inductively coupled plasma-optical emission spectroscopy (ICP-OES, JobinYvon 238 Ultrace, Instruments S.A. GmbH, D-85630 Grasbrunn) after aqua regia digestion according to DIN EN ISO 15587-1 and DIN EN ISO 17294-2 by the Institute of conservation and quality assurance (IUQ). The citric acid extractable P (P_{ca}) was determined using citric acid (2% v/v) and a fertilizer/solution ratio of 1:10 (VDLUFA, 2007). The recycled products and TSP were sequentially extracted according to a modified Hedley procedure (Hedley et al., 1982). In brief, 0.5 g of the products was added to 30 mL of distilled water (H_2O- P_i) and shaken for 16 h on a horizontal shaker at 150 rpm. The solution was centrifuged for 20 min at 3500 rpm, and the supernatant was decanted. The same procedure was used for subsequent extractions with 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1 M H_2SO_4. The P_{tot} in the supernatant of each fraction was measured using ICP-OES. Oxalate-extractable Fe_{ox}, Al_{ox}, and P_{ox} in the recycled products and TSP were determined according to Dayton and Basta (2005) by shaking 1 g of the product with 100 mL of acid ammonium oxalate in the dark for 1 h. The P, Al, and Fe concentrations were measured using ICP-OES at wavelengths of 214.914 nm (P), 396.152 nm (Al), and 259.940 nm (Fe). The concentrations of Fe_{ox}, Al_{ox}, and P_{ox} were also measured in the soil by using a ratio of 2:100 soil to oxalate solution (Schwertmann, 1964). With these values the P-sorption capacity (PSC [mmol kg^{-1}] = (Al_{ox} + Fe_{ox}) x 0.5) and the degree of P saturation (DPS [%] = P_{ox} / PSC x 100) were calculated according to Lookman et al. (1995). The water-soluble P (P_w) in soil was determined according to Van der Paauw (1971). The concentration of double lactate extractable P (P_{dl}) and the pH value of the soil (0.01 M $CaCl_2$) were analyzed according to Blume et al. (2010).

2.3.3 P XANES data collection and treatment

All P K-edge XANES experiments were conducted on the Soft X-Ray Micro characterization beamline (SXRMB) at the Canadian Light Source in Saskatoon, Saskatchewan, Canada, which is equipped with a Si(111)double-crystal monochromator covering an energy range of 2 to 10 keV and has a 4-element Si(Li) drift detector for fluorescence measurements. The beamline energy was calibrated using Ar K-edge around 3205 eV; this means that the main peak position of Al phosphate ($AlPO_4$) was around 2152.9 eV. All soil samples were air-dried and ground in an agate stone mortar before being spread as a thin film onto a P-free carbon tape that was mounted onto a copper sample holder. All spectra were recorded in fluorescence yield mode at photon energies between 2130 and 2210 eV (P K-edge). The step size was 1 eV in the pre-edge region (2130 to 2140 eV), 0.25 eV at the edge step (2140 to 2180 eV), and 0.5 in the post-edge region (2180 to 2200 eV) using a dwell time of 1 s. At least three scans were averaged. All spectra were normalized to the intensity of the incident beam, which was measured at the same time as the current was emitted from a gold mesh. In order to reduce beam damage, the position of the beam was slightly moved after each scan, thereby always hitting a “fresh” sample spot. Background and baseline correction of the P K-edge spectra was done using ATHENA (Ravel and Newville, 2005).

2.3.4 Statistical analyses

For statistical analyses the software package PASW Statistics 18 was used. Data corresponding to three replications were subjected to an analysis of variance (ANOVA, general linear model). The means of soil parameters were compared by the Duncan multiple range test. Significance was determined at $p < 0.05$, and significantly different means were indicated by using different letters.

2.4 RESULTS AND DISCUSSION

2.4.1 Composition of the recycled products and TSP

2.4.1.1 Nutrient and heavy metal concentrations

The concentration of nutrients and heavy metals differed widely among the test materials (Table 2-2). Differences in elemental composition can be explained by differences in the origin and composition of the raw materials, as well as by production processes and subsequent chemical treatments. Concentrations of Al, Ca, and Mg were highest in the recycled products receiving the respective additions of $Al_2(SO_4)_3$ (Al-SSA, Al(ut)-SSA) during P precipitation, $CaCl_2$ (Ca-SSA) and $MgCl_2$(Mg-SSA) during the thermo-chemical treatment, or $MgCl_2$ for the precipitation of struvite. High Al concentration in Al-based SSAs can increase the concentration in amorphous Al in soil, which can lead to toxic effects for crops (Kochian, 1995; Oladeji et al., 2009) or to an elevation of the P sorption capacity in soil (Krogstadt et al., 2005; Bøen, 2013) (see “Incubation Experiment”, below). During the full H_2SO_4 digestion for the Al-SSA, Al compounds are also dissolved and are found to be X-ray amorphous (Petzet et al., 2012). This is consistent with the high concentration of Al_{ox} and Fe_{ox} measured in the Al-SSA, which reached almost 100% of total Al and Fe concentration (Table 2-2). The lower concentration of Al_{ox} and Fe_{ox} in the thermo-chemically treated SSAs is because of their lower Al and Fe concentrations and the partial H_2SO_4 digestion. Among all recycled products only struvite contained N.

Table 2-2 Total nutrient and heavy metal concentrations, concentration of oxalate soluble Al (Alox) and Fe (Feox), and pH values of the recycled products and triple superphosphate (TSP).

	K	Mg	Ca	N	Al	Fe	Al_{ox}	Fe_{ox}	pH
g kg^{-1}									
Al-(ut)SSA	9.5	15.1	76.1	-	95.6	20.6	56.4	11.6	11.2
Al-SSA	5.1	7.7	42.6	-	55.8	10.4	54.1	10.3	1.9
1Ca-SSA	4.4	15.0	96.1	-	26.2	54.5	12.7	3.7	3.9
2Ca-SSA	4.1	9.3	96.9	-	23.9	29.2	11.5	3.0	3.6
1Mg-SSA	7.9	52.2	61.2	-	17.9	43.5	8.7	11.2	5.1
2Mg-SSA	4.8	49.1	54.3	-	17.1	38.1	8.6	4.8	4.0
Struvite	0.6	93.4	4.9	41.7	39.6	18.5	0.1	1.9	7.5
TSP	-	8.9	106.7	-	29.4	22.5	0.0	0.1	2.3
	Cd	Pb	Ni	Cu	Zn	Hg	As	Cr	
mg kg^{-1}									
Al-(ut)SSA	3.6	153	67	1480	3140	0.1	8.4	62	
Al-SSA	2.3	93	43	813	1820	0.1	6.0	38	
1Ca-SSA	<0.1	20	102	103	117	<0.1	4.1	106	
2Ca-SSA	0.3	28	83	101	143	<0.1	9.5	150	
1Mg-SSA	0.4	15	96	193	299	<0.1	3.1	101	
2Mg-SSA	0.4	27	89	286	548	<0.1	10.7	123	
Struvite	0.2	2.7	18	35	42	<0.1	0.2	93	
TSP	26.0	<0.1	4	13	65	<0.1	5.3	60	

SSA= sewage sludge ashes, ut= untreated

None of the tested products exceeded the European Union limit values for concentrations of heavy metals in sewage sludge laid down in Council Directive 86/276/EEC (Annex 1b) of June 12, 1986. However, some of the products contained levels of heavy metals which exceed the limiting values of current regulations in several European member states (Hukari et al., 2016), including the cadmium (Cd) content in TSP, lead (Pb) in Al(ut)-SSA, and nickel (Ni) for the treated SSAs. The highest Cd concentration was found for TSP (26 mg kg^{-1}), which is in the range of the values measured by Mahdy (2012) and Siebers et al. (2013). The Cd concentration in the recycled products, however, was only 0.1 to 3.6 mg kg^{-1}. Even related to the respective P_{tot} concentration, the Cd concentration of TSP was still 7 (Al-(ut)-SSA) to 130 (struvite) times higher than in the recycled products. Therefore, the continuous usage of P fertilizers produced from PR sources poses the risk of soil contamination (Siebers and Leinweber, 2013) and accumulation in plant tissue, as Cd can readily be taken up by plants because of its high mobility (Uraguchi et al., 2009). Except for chromium (Cr), struvite had the lowest concentration of heavy metals among all products. This is because heavy metals are not involved in the crystallization process of struvite, and significant co-precipitation or adsorption reactions do not take place (Kern et al., 2008).

Acidic pH values were determined in all treated SSAs and TSP, while alkaline pH values were measured for Al(ut)-SSA and struvite. Usually biomass ashes have a liming effect due to their high pH values (Nanzer et al., 2014a; Schiemenz and Eichler-Löbermann, 2010). The observed low pH of the treated SSA can be explained by the H_2SO_4 digestion. The alkaline pH value found for struvite is a result of the aeration in the reactor increasing the pH up to 8 during the precipitation process (Kern et al., 2008).

2.4.1.2 Extracted P fractions

The recycled products and TSP differed in their P_{tot} concentration (Table 2-1, Figure 2-1), with the highest Pt concentration found for TSP (178.2 g P kg^{-1}) followed by struvite > Al(ut)-SSA > 2Mg-SSA > 2Ca-SSA > Al-SSA > 1Ca-SSA > 1Mg-SSA. The P_{tot} values are related to the P concentrations in the raw material used and also to the recycling processes. Thus, the lower P_{tot} concentration of the Al-SSA compared to the Al(ut)-SSA is related to P losses during the H_2SO_4 treatment and subsequent removal of co-dissolved heavy metals from the dissolved P (Petzet et al., 2011; Petzet et al., 2012). However, the P_{tot} concentration alone is not a suitable indicator for the fertilizer quality. Therefore, the P composition of the recycled products and TSP were further analyzed in order to estimate P fractions of different availability.

In a first step, citric acid P extraction (P_{ca}), which mimics root exudation (Nelson et al., 1953), was used to determine the plant-available proportions of P_{tot} in the recycled products (Table 2-1). The highest P_{ca} concentration was found for TSP (100% of P_{tot}), which is in line with the high acid solubility of its main component, $Ca(H_2PO_4)_2$. Among the recycled products the proportion of P_{ca} on P_{tot} was in the range of 30% to 88% and followed a different order than Pt: struvite > 1Mg-SSA, 2Mg-SSA, Al-SSA > 1Ca-SSA, 2Ca-SSA > Al(ut)-SSA.

The low Pca concentration of Al(ut)-SSA might indicate the formation of citric-acid-insoluble Al-P phases during the wastewater treatment and incineration (Petzet et al., 2012; Krüger and Adam, 2015). The lower P_{ca} concentration in both Ca-SSAs compared to the other treated SSAs is in agreement with Nanzer et al. (2014b) and could be a result of the higher crystallinity and thermo-dynamic stability of the formed P phases in the Ca-SSAs. Kratz et al. (2010) tested various methods to predict the P fertilizer effect of about 160 P-containing products and obtained comparable results for the extractions with ammonium citrate and with citric acid.

Next, the sequential P fractionation was applied to further differentiate the P fractions in the recycled products according to their solubility (Table 2-1, Figure 2-1). The H_2O-P and the $NaHCO_3$-P fractions generally represent labile and highly soluble P forms, which are immediately plant available, whereas the NaOH and H_2SO_4 fractions are considered to represent P forms of moderate to low solubility (Hedley et al., 1982). In Table 2-1 and Figure 2-1 only the inorganic P forms (P_i) are presented. Due to the incineration process, the organic P (P_o) compounds in the sewage sludge were thermally destroyed and converted to P_i forms in the SSAs (Donatello and Cheeseman, 2013; Nanzer et al., 2014a). The P_o content in struvite could be neglected as well ($NaHCO_3$-P_o: 0.86 g kg^{-1}, NaOH-P_o: 1.88 g kg^{-1}).

The proportions of H_2O-P at P_{tot} varied from 0.1% for Al-(ut)SSA to 83% for TSP (Table 2-1, Figure 2-1). The variations of the H_2O-P_i concentration within the acidic treated SSAs is related to the quantity of H_2SO_4 added (Petzet et al., 2012). Thus, the lower P solubility of 1Ca-SSA compared with 2Ca-SSA, as well as of 1Mg-SSA compared with 2Mg-SSA, can be explained by the lower H_2SO_4 addition per unit P during the production process. The low proportion of H_2O-P in struvite (3% of P_t) was in agreement with other published values (e.g., Johnston and Richards, 2003; Römer, 2006; Cabeza et al., 2011). The proportion of $NaHCO_3$-P of all tested products was lower compared with the other fractions exhibiting proportions only 0.3% to 6%. This indicates that the highly soluble P is mainly present in the H_2O-P fraction. For Al(ut)-SSA and struvite both the H_2O-P fraction and the $NaHCO_3$-P fraction were low. The low values for Al(ut)-SSA can be explained by the missing H_2SO_4 treatment, as described above. The low solubility of struvite in $NaHCO_3$ is most likely explained by the pH of 8.5 of this extractant, which is in the range of pH 7 to 11.5 in which struvite precipitates (Rahman et al., 2014; Harrison et al., 2011). The low concentration in the labile Hedley fractions for struvite is in contrast to the high P solubility in citric acid, and the content of bioavailable P in soil after struvite application (Vogel et al., 2015). This indicates that neutral or mild alkaline extractants drastically underestimate the P availability of struvite (see also Incubation experiment below).

Sodium hydroxide extracts P, which is most likely bound on Al- and Fe-(hydr)oxides and in organic molecules (He et al., 2005). A high proportion of NaOH-Pi was found for Al-SSA (34%), 1Mg-SSA (29%), and Al(ut)-SSA (24%), which is in agreement with the high Fe_{ox}/P_{ox} and Al_{ox}/ P_{ox} ratios of these products (Table 2-2). Nanzer et al. (2014a) also indicated a high NaOH-P concentration in SSAs, where Al or Fe salts were used for P precipitating during wastewater treatment. The NaOH-P concentration of struvite (14%) was in the midrange of all products tested. Sparingly soluble Al-/Fe-phosphates are also formed under alkaline conditions along with the struvite precipitation (Rahman et al, 2014). In addition Harrison et al. (2011) found a relatively high P solubility of struvite in strongly alkaline solutions, which is true for 0.1M-NaOH (pH: 13).

The proportions of the H_2SO_4-P fraction from P_{tot} in the SSAs were 21% (2Mg-SSA) to 75% (Al(ut)-SSA) and in the range of the proportions for other raw SSAs extracted with HCl (Nanzer et al., 2014a). This P fraction represents complex compounds of P with Ca and Mg and is therefore related to the Ca and Mg concentrations of the ashes (Table 2-2). A subsequent H_2SO_4 treatment of the SSAs dissolved these P forms and removed unwanted Ca^{2+} by controlled precipitation of gypsum ($CaSO_4 \, 2H_2O$) and led to the formation of more-soluble Ca-P and Mg-P forms (Petzet et al., 2012), which is reflected in the lower proportions of H_2SO_4-P in Al-SSA compared to Al(ut)-SSA. The proportion of P in the H_2SO_4-P fraction of the thermo-chemically treated SSAs was about one-third of P_{tot} (20 to 40%). The addition of $MgCl_2$ (Mg-SSA) or CaCl2 (Ca-SSA) as a chlorine donor to remove the heavy metals from the ash resulted in the formation of poorly soluble P compounds such as chlorapatite (Nanzer et al., 2014a), which was not completely decomposed by the partial H_2SO_4 treatment. The H_2SO_4-P made up the highest proportion in struvite, which can be explained by the low solubility of struvite in mild extractants with a pH of 7 to 11 (see above). The solubility of P in struvite is better in acid extractants, as also found for citric acid. Several authors confirmed the high P solubility of struvite in acidic solutions (Harrison et al., 2011; Rahman et al., 2014).

2.4.1.3 P K-edge XANES

Phosphorus K-edge XANES spectroscopy was applied to further characterize the P composition of the different recycled products in the solid phase without the risk of chemical changes due to chemical extraction (Fig. 2-2). The unusually low ratio between the intensities of the white line and the edge step indicated that P K-edge spectra may have been influenced by self-absorption despite all samples having been applied on the sample holder as a very thin film. Furthermore, background effects from sample matrices cannot be ruled out. Therefore, P K-edge XANES spectra evaluation by linear combination fitting (LCF) or partial least square regression could not be applied, as pre-tests yielded unrealistic P compositions with unacceptably high residuals (data not shown).

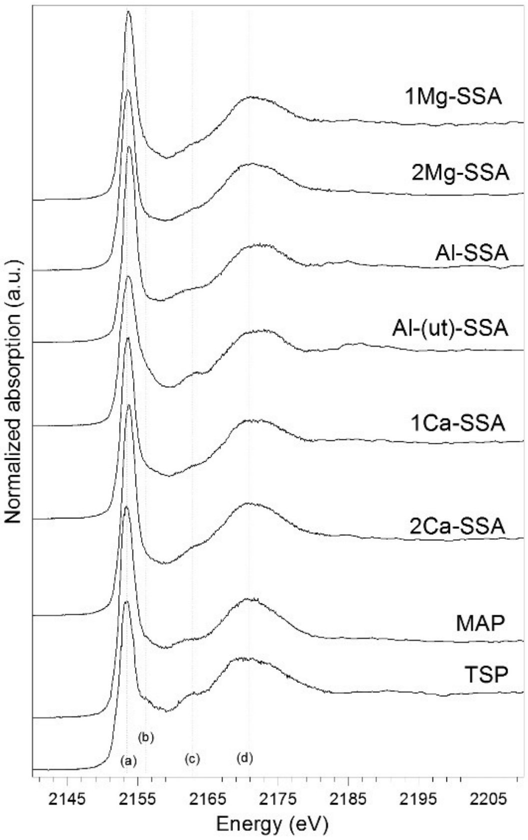

Figure 2-2 Stacked P K-edge XANES the recycled products and triple superphosphate (TSP). SSA= sewage sludge ash, MAP= struvite, ut= untreated.

For this reason spectra were interpreted based on visual comparison with P reference standards recorded in this study or published elsewhere, as reviewed by Kruse at al. (2015). All SSA K-edge spectra were very similar in shape and were characterized by a main peak (a) at ~2153.7 eV, indicating the dominance of P^V in the form of phosphate in all SSAs. This peak appeared at slightly lower energies (2153.4 eV) in the spectra of struvite and TSP.

The second main peak (d) (oxygen oscillation) showed some subtle variation in shape and position and appeared at ~2171.5 eV. The lack of a pre-edge peak – characteristic for Fe-associated P (Hesterberg et al., 1999, Khare et al., 2004) – indicated that Fe-P was not present in significant proportions in any of the investigated SSAs despite some of the SSAs (Al(ut)-SSA, Al-SSA, and 1Mg-SSA) having relatively high total Fe concentrations (Table 2-2). The spectrum of TSP showed typical spectral features from Ca-associated P, the chemical sensitivity of P K-edge XANES spectroscopy was not high enough to resolve the P speciation within these complex materials.

2.4.2 Incubation Experiment

2.4.2.1 Soil pH

The products affected the soil pH and for most of the treatments a decrease in soil pH was found compared to the control treatment (Figure 2-3, Supplemental Table 6-1). The decrease in soil pH after the addition of the treated SSAs compared to the control (pH about 5.66) is related to their low pH (Table 2-2) due to digestion with H_2SO_4. Hence, the decrease of the pH from the first day after incubation (1.6 units) until the end of the experiment (1.3 units) was most pronounced for the Al-SSA, as this ash had the lowest pH value of all SSAs due to the complete digestion with H_2SO_4. This sharp drop in the soil pH needs to be considered when using untreated SSAs as fertilizer. For the thermochemically treated SSAs, which were only partially digested with H_2SO_4, the reduction of soil pH in comparison to the control was lower (only 0.2 to 0.3 units). In contrast, soil pH increased due to struvite application (0.6 units) as a consequence of its neutral to alkaline pH of 7.5. The only treatment where the pH of the product was not consistent with the change in soil pH after its application was the Al(ut)-SSA treatment. Here the soil pH was in the range of the control in spite of its alkaline pH of 11.2 of Al(ut)-SSA. This could be explained by its high concentration of Al^{3+}, which is known to enhance acidity in soil (Blume et al. 2010). The concentration of Al_{ox} in soil increased after the application of the Al(ut)-SSA (Al_{ox}: 820 g kg^{-1}) compared to the control (Al_{ox}: 661 g kg^{-1}) (Al_{ox} and Fe_{ox} data of the soil not shown). The changes in pH during incubation time were relatively small but significant because of the low standard deviation of the pH values.

2.4.2.2 Readily available P concentrations in soil

The dissolution kinetics were generally fast, and the application of recycled products and TSP affected the P fractions in soil after just one day of incubation, followed by only slight changes during the complete incubation study.

The Pw pool in soil strongly increased after the application of the fertilizer treatments with the exception of the Al(ut)-SSA treatment, which was in the same range as the control (13.5 mg kg^{-1}, average of all sampling dates) (Figure 2-2, Supplemental Table 6-2). For TSP (163.6 mg kg^{-1}), struvite (136.7 mg kg^{-1}), and 2Mg-SSA (123.0 mg kg^{-1}), Pw values were almost 10 times higher (after 1 wk of incubation) than for the control. The Pdl values in the soil were also considerably higher after the application of the products and showed a similar order as the Pw concentrations after one week of incubation time: struvite (377.3) > TSP (299.9) > 2Mg-SSA (246.0) > 1Mg-SSA (193.4) = Al-SSA (182.4) > 2Ca-SSA (136.9) > 1Ca-SSA (99.2) > Al(ut)-SSA (75.7) > CON (50.0) (all values in mg kg^{-1}). The high Pw concentration in soil after the application of TSP and 2Mg-SSA is in agreement with the high percentage of H_2O-P from Pt found by the sequential extraction (Figure 2-1). The fast increase in the Pw concentration in soil after the application of struvite, however, is in contrast to the low values of the H_2O-P fraction found by sequential extraction. The acid soil conditions, which were below the suitable pH for struvite precipitation (see below), resulted in a very fast dissolution of the initially water-insoluble P compounds in struvite and in a release into the soil P_w fraction from the first day of incubation. Because of its low solubility in water, struvite is sometimes considered to be a slow-release P fertilizer (Rahman et al., 2011). However, the results of this study instead point to rapid dissolution of P from struvite and a fast effect on plant nutrition on acid soils. This high P release from struvite after one day of incubation is also in accordance with Cabeza et al. (2011), who found that after the application of struvite the P concentration in the soil solution was comparable to TSP in neutral to acidic soils after several hours. A fast dissolution of P from struvite was also assumed in pot experiments with slightly acid soil by Bonvin et al. (2015) and Vogel et al. (2015).

The study of Talboys et al. (2016) also underlined the enhanced solubility of struvite in the presence of organic acid anions and lower pH values. In alkaline soil the P release of struvite and the fertilizer effect may be deferred due to lower initial solubility of the struvite (Ackerman et al. 2013). The low P_w and P_{dl} concentration in soil in the Al(ut)-SSA treatment can be explained by its composition, as it mainly consists of poorly soluble P compounds (see sequential extraction and XANES analyses, Figure 2-1and Figure 2-2).

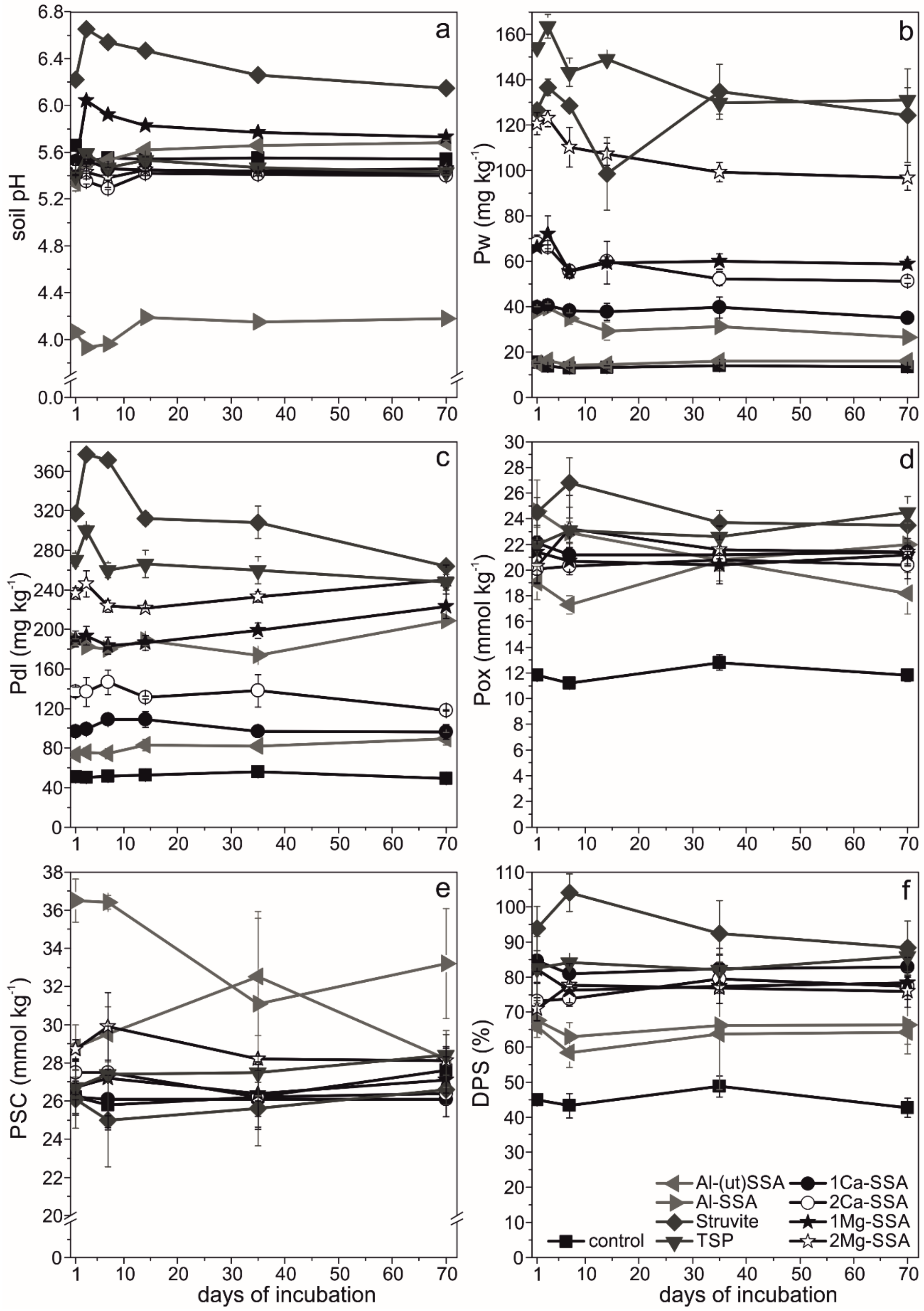

Figure 2-3 Effects of the recycled products and triple superphosphate (TSP) on the (a) pH value, (b) water-soluble P (Pw), (c) double lactate-soluble P (Pdl), (d) oxalate soluble phosphorus (Pox), (e) P sorption capacity (PSC), and (f) degree of P saturation (DPS) of the soil after 1, 3, 7, 14, 35, and 70 days of incubation. DPS, and PSC were investigated at four sampling dates only. SSA= sewage sludge ash, TSP= tripe superphosphate, ut= untreated.

A complete H_2SO_4 digestion increased the P solubility of Al-based SSAs and resulted in higher P_w and P_{dl} concentrations in soil in the Al-SSA treatment. Among the thermo-chemically treated SSAs, the application of Ca-SSAs resulted in concentrations of readily soluble P in soil that were only half those for Mg-SSAs.

This is related to their composition (see section 3.1.2) and to their behavior in soil. Vogel et al. (2013) and Römer (2006) described the different reactions of Ca and Mg-pyrophosphate in the soil; mainly Mg-pyrophosphate formed plant-available P phases. The changes of the bioavailable P pools during the incubation time were relatively small, which was also stated by Massey et al. (2009) for TSP, struvite, and Mg phosphate.

However, the P_w and P_{dl} concentrations in soil slightly decreased for most the treatments (Al-SSA, 2CA-SSA, 1Mg-SSA, 2Mg-SSA, and TSP) in comparison to the values after the first three days of incubation, which could be related to the formation of less-soluble dicalcium phosphate or even tricalcium phosphate over time (Vogel, 2013).

In the present study one cannot determine whether the P in the bioavailable soil fractions derived from the soil or from the fertilizer product. The products applied can support or inhibit the P dissolution from soil resources as a result of changes in soil properties like pH and PSC. To get concrete information about the source of the P in the bioavailable P fractions a radioisotope approach is needed, as done, for example, by Bonvin et al. (2015).

2.4.2.3 P sorption capacity and degree of P saturation

The oxalate-soluble P, Al, and Fe concentrations in soil and the subsequent calculation of PSC and DPS were done for four sampling dates only (1, 7, 35, and 70 days of incubation) (Figure 2-3, Supplemental Tables 6-3). The P_{ox} values, which represent the P adsorbed to Al- and Fe-oxide, followed a similar pattern as the P_w and P_{dl} values, although oxalate is a stronger extractant and more P was released with this method. In the treatments with P application, the P_{ox} values almost doubled in comparison to the control (670 vs. 370 mg per kg or 21.5 vs. 12 mmol, average values for all fertilizer treatments at the end of the experiment). High values were measured for the TSP and struvite treatments and low values for the control and Al-(ut)SSA.

The PSC values were calculated on the basis of the Al_{ox} and Fe_{ox} concentrations in soil and were found to be highest in soil after the application of the Al-SSA (34.3 mmol kg^{-1}, average of all sampling dates). This is in accordance with the high concentrations of Al_{ox} and Fe_{ox} in the Al-SSA (Table 2-2). The Al(ut)-SSA ash also contained considerable amounts of Al_{ox} and Fe_{ox}, but because of its high P_{tot} concentration (Table 2-1) less ash (and as a result less

Al_{ox} and Fe_{ox}) was applied to the soil to reach the P application dose of 400 mg kg^{-1} soil. Subsequently, PSC values in the Al(ut)-SSA treatment (29.7 mmol kg^{-1}) were lower than in the Al-SSA treatment but still higher than the control (26.4 mmol kg^{-1}) (average of all sampling dates). The PSC is also related to soil characteristics, and negative correlations were found between pH and PSC (-0.668, $p < 0.01$) and between P_{dl} and PSC (-0.699, $p < 0.01$). Negative correlations were also found between PSC and other European soil P tests (Börling et al., 2004), which indicates that high PSC values can limit the available P concentration in soil and the plant P uptake.

Due to the application of the recycled products and TSP, a strong increase of the P saturation was found compared with the control (44.9%), and, on average of all sampling dates, between 63.0% (Al(ut)-SSA) and 94.6% (struvite) was reached (Figure 2-3). These high values can be explained by the high amount of P applied to the soil with the recycled products (400 mg kg^{-1} soil) and the relatively small initial Al_{ox} and Fe_{ox} concentration in the soil. According to Lookman et al. (1996) and Beauchemin and Simard (1999), 40% is the threshold from which DPS increases exponentially with the subsequent addition of P. The DPS values in soil after application of both Al ashes were about 10 to 20% lower than in the other fertilizer treatments, which is related to the high soil PSC in the case of Al-SSA and the low P_{ox} in soil in the case of Al(ut)-SSA. These results indicate that the DPS depends on the amount of P applied and its behavior in soil, as well as on the type of P source and its concentration of oxalate-soluble Al and/or Fe. Like the other values measured in the soil, the DPS was only marginally affected by incubation time.

2.5 CONCLUSIONS

Chemical analysis of recycled products is necessary to obtain information about their composition, but fertilizer quality may be misjudged if the behavior of the products in soil is not also considered. Sequential fractionation showed low values in the labile P fractions (H_2O-P, $NaHCO_3$-P) of struvite, although in the incubation experiment the plant-available P pool was higher after struvite application than after the application of all other tested products, which points to a high P fertilizer potential of struvite.

An assessment of recycled fertilizers regarding the P sorption and P losses on noncalcareous soils should include the analysis of P forms, the concentration of amorphous metal oxides, and pH. Aluminum-based precipitating agents can increase the concentration of Al_{ox} in the recycled products, which in turn results in higher P sorption and, subsequently, lower P availability to plants, but also in lower risk of P losses. Under acidic soil conditions, TSP, 2Mg-SSA, and struvite application resulted in high concentrations of water-soluble P in soil, as well as in high degrees of P saturation from the first day of incubation. Although struvite is frequently considered as a slow-release P source, P leaching can be expected when struvite is applied in large quantities to acid soils.

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3 PHOSPHORUS APPLICATION WITH RECYCLED PRODUCTS FROM MUNICIPAL WASTEWATER TO DIFFERENT CROP SPECIES

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3.1 ABSTRACT

In this study, the phosphorus (P) fertilizing effects of struvite, one thermochemical treated sewage sludge ash (SSA) based on Ca-P (Ca-SSA) and one full sulfuric acid-digested SSA based on Al-P (Al-SSA) were analysed in comparison to triple superphosphate (TSP) and a control treatment (CON) without P application in a two-year field experiment. In the field experiment, the effects of the recycled products on crop yield, P uptake and labile soil P fractions were analysed. In addition, the effect of nitrogen and magnesium contained in struvite was investigated in the second year of the experiment compared to TSP and CON. In the first year, spring barley was cultivated in the field experiment; and in the second year, it was forage rye followed by sorghum. In the second year, the relative P effectiveness (forage rye, sorghum) of the recycled products compared to TSP increased in the order: Ca-SSA (81%, 91%) ≤ Al-SSA (91%, 96%) = struvite (102%, 110%). In addition, an magnesium fertilizing effect of struvite could be demonstrated. The results show that the recycled products from wastewater treatment are appropriate to substitute rock phosphate-based fertilizers.

3.2 INTRODUCTION

Currently, mainly mined phosphate rock (PR) is used as phosphorus (P) fertilizer in agriculture, but global PR resources are limited and moreover primarily found in politically unstable regions (Jasinski, 2014). Secondary phosphate resources like animal slurries and manure as well as residues from bioenergy production, ashes, bone and meat meal are commonly used to provide P to agricultural fields (Bachmann et al., 2011; Eichler-Löbermann et al., 2007; Reijnders, 2014; Vassilev et al., 2013). Municipal wastewater however is also a promising P resource, incurring about 3 MT of P globally each year (Elser, 2012). Sewage sludge products or sediment from wastewater treatment plants can be used directly after hygienization as P fertilizer (Tuszynska et al., 2013), but the direct application of sewage sludge as fertilizer is declining in Europe since untreated sludge may contain high concentrations of harmful substances (Renner, 2000; Nanzer et al., 2014a). The organic contaminants in sewage sludge can be destroyed by incineration, but after incineration heavy metals are enriched in the resulting sewage sludge ash (SSA) and the P solubility of SSA is usually low (Franz, 2008). Therefore, several new recycling processes have been developed during the last years to separate heavy metals and to improve the P solubility of SSAs (Adam et al., 2009; Sartorius et al., 2012; Donatello and Cheese-man, 2013). Among others, acid or alkaline leaching can be applied to improve the P solubility (Petzet et al., 2012). The thermo-chemical treatment of SSAs, whereby chloride (Mg-Cl2, Ca-Cl2) is added to the ash at about 1000°C to produce a metal-depleted solid residue, was described as a promising approach by Mattenberger et al. (2008) and Adam et al. (2009). After these treatments, heavy metal concentrations in SSAs usually undercut the European (EU) limit values for concentrations of heavy metals in sewage sludge products (Council Directive 86/276/EEC). Another promising example of P recovery from sewage is struvite ($MgNH_4PO_4$ $6H_2O$, magnesium ammonium phosphate). Struvite contains only small amounts of harmful substances and is characterized by relatively high P solubility (Johnston and Richards, 2003; Kern et al., 2008; Rahman et al., 2014). The P solubility of the wastewater products differ according to their chemical P composition, which in turn is influenced by the salt used for P precipitation and the kind of chemical treatment (Phan et al., 2009). However, the P fertilizer effect of these products also depends on soil characteristics. Nutrient uptake efficiency and mobilization mechanisms of crops are also important for high utilization of applied P (Richardson et al., 2011) and tests regarding the P availability for different crops are required to improve the production process and consequently the quality of these products. The effects of struvite and other precipitated phosphates have been tested in pot experiments with perennial ryegrass (Johnston and Richards, 2003) and rye (Römer, 2006) on different soils. On loamy sands struvite was evaluated by Gonzalez-Ponce et al. (2009) when applied to lettuce and by Massey et al. (2009) to spring wheat. Results showed especially for struvite a good efficacy which was comparable to highly soluble commercial P fertilizers. For thermo-chemically treated and H_2SO_4-digested SSAs, positive effects on ryegrass were observed by Nanzer et al. (2014b) and Severin et al. (2013). Although these studies showed a general potential of P recycled products to increase crop growth and nutrient uptake, investigations concerning interactions of different P recycled products and various crops are rarely available. Beside the effect of the P recycled products on plant growth, investigations regarding their effects on soil P pools are of interest as well and contribute to an understanding of the transformation processes of applied P in the soil. The sequential extraction is a common wet chemical method (Hedley et al., 1982; Thiessen and Moir, 1993), whereby different P fractions of decreasing bioavailability become extracted step by step by using stronger extracting agents. This allows the investigation of the effect of P products and crop species on soil P cycles, and also provides information about the pathway of remaining P in the soil and helps to predict its prospective availability. In this study, two greenhouse experiments were carried out to determine the P fertilizing effect of different P recycled products including a solar-dried sewage sludge (SSS), an untreated SSA, a H_2SO_4-digested SSA, four thermo-chemically treated SSAs, and struvite. The wastewater products were compared with a common rock-phosphate-based P fertilizer, triple superphosphate (TSP), and a control (CON) without P application. Five different crops including monocot and dicot species (maize, forage rye, sorghum, amaranth, and sunflowers) were included in this study. Maize was cultivated in both experiments. The aim of this study was to compare the effect of the P recycled products on (1) P availability for crops, (2) crop yield, and (3) on soil P pools as well as to determine the interactions between the fertilizer treatments and the cultivated crops.

3.3 MATERIALS AND METHODS

3.3.1 Fertilizer treatments and experimental design

Two pot experiments were carried out, a main experiment including four different crops and a control experiment including two different crops. Maize was cultivated in both. The control experiment (2012) was conducted to verify the results of the main experiment (2011). In both experiments the same fertilizer treatments were applied (see below). The soils used were moderately acidic loamy sands and according to the World Reference Base for Soil Resources, the soil is classified as Stagnic Cambisol. The soils were collected from the A horizon of a field experiment from the experimental station of the University of Rostock. The double lactate (dl) soluble P (Pdl) concentrations were below 56 mg kg^{-1} soil, indicating a suboptimal P supply for plants according to the German soil-P classification. The soil characteristics of the soil in both years were similar, since it was collected from the same field (soil 2011 vs. 2012: P_{dl} 40.1 vs. 48.0, Mg_{dl} 120 vs 147, K_{dl} 61.2 vs. 63.5, Pt 515 vs 517 (all values in mg per kg soil), pH 5.19 vs. 5.29, soil organic matter 2.31 vs. 2.38%). In both experiments, 6 kg of air-dried and sieved (2 mm) soil was filled into Mitscherlich pots. The soils were amended with the recycled P products, or highly soluble mineral P in the form of triple superphosphate (TSP) at a rate equivalent to 200 mg P per pot. In addition, a control treatment without P application was carried out (CON). Since with the treatments also other nutrients beside P were applied (see Table 3-1), the addition of N, K, and Mg was adapted to ensure a uniform supply of these nutrients to all treatments according to the following amounts per pot: N: 0.5 g, K: 1.0 g, and Mg: 0.3 g with nutrient salts. Beside the TSP and the control treatment eight recycled P products remaining from wastewater treatment were applied. A solar-dried sewage sludge (SSS) was produced by solar radiation in a greenhouse, assisted by a turning and conveying machine, yielding granulate of about 10 mm with a dry matter concentration of up to 90%. The precipitating agent used in the sludge was iron (Fe) salt. Furthermore, untreated and treated sewage sludge ashes (SSA) were applied (the nomenclature was done according to the main P binding form in the ashes). For the untreated ash, sewage sludge was mono incinerated, whereat P was precipitated in the wastewater with aluminum salt (Al(ut)-SSA). The five treated SSAs also based on mono incinerated sludge but these ashes were further treated to improve the bioavailability of P and to reduce the concentration of heavy metals. For Al-SSA, P was also precipitated in the wastewater with Al before the sludge was mono incinerated. The ash was then treated by a H_2SO_4-washing procedure and 300 g H_2SO_4 (96%) per kg SSA was added to increase the P availability. The other four SSAs were thermo-chemically treated, whereby heavy metals were evaporated in a rotary furnace at a temperature of 1000°C after the addition of $MgCl_2$ (Mg-SSA) or $CaCl_2$ (Ca-SSA) as a chlorine donor at a rate of 100 mg kg^{-1} ash. Afterwards, 30% H_2SO_4 was added to increase the P availability. A more detailed description of the process can be found in Mattenberger et al. (2008) and Adam et al. (2009). The raw sewage sludges used to produce the two Mg-SSAs and Ca-SSAs were derived from different batches from the same wastewater treatment plant and had different concentrations of P and other nutrients (Table 3-1). The P solubility of the four thermo-chemically treated SSAs, were also different, because H_2SO_4 was added per kg SSA and not per P unit. The struvite (magnesium ammonium phosphate, MAP) was produced according to a process developed by Berliner Wasserbetriebe (BWB), where the digested sludge is aerated in a reactor to raise the pH up to 8 for MAP precipitation by stripping CO_2 and adding $MgCl_2$ (Kern et al.,2008).

Table 3-1 Application rate (g per pot), element concentration (g kg^{-1}) and pH values of the recycled products and TSP.

	Rate	P_t	P_{ca}	K	Mg	Ca	N	Al	Fe	Al_{ox}	Fe_{ox}	pH
	g pot^{-1}	g kg^{-1}										
SSS	6.5	30.6	22.4	1.9	3.8	19.3	19.0	15.5	35.4	n.a.	n.a.	6.5
Al(ut)-SSA	2.0	98.6	29.9	9.5	15.1	76.1	-	95.6	20.6	56.4	11.6	11.2
Al-SSA	3.4	58.5	45.9	5.1	7.7	42.6	-	55.8	10.4	54.1	10.3	1.9
1Ca-SSA	4.5	44.4	29.1	4.4	15.0	96.1	-	26.2	54.5	12.7	3.7	3.9
2Ca-SSA	3.2	62.4	46.0	4.1	9.3	96.9	-	23.9	29.2	11.5	3.0	3.6
1Mg-SSA	5.1	39.4	34.5	7.9	52.2	61.2	-	17.9	43.5	8.7	11.2	5.1
2Mg-SSA	3.0	65.9	44.0	4.8	49.1	54.3	-	17.1	38.1	8.6	4.8	4.0
Struvite	1.8	121.7	102.7	0.6	93.4	4.9	41.7	39.6	18.5	0.1	1.9	7.5
TSP	1.2	157.0	168.9	n.d.	8.9	106.7	-	29.4	22.5	0.0	0.1	2.3

Pt = total P, Pca = P soluble in citric acid, Alox, Feox = oxalate soluble Al and Fe, SSS = solar dried sewage sludge, SSA = sewage sludge ashes, ut = untreated, TSP = triple superphosphate, n.a. = not analyzed.

The wastewater products differed in total P (Pt) concentration and P solubility (citric acid soluble P (Pca) (see Table 3-1). Highly soluble triple superphosphate (TSP) as one of the most used rock-phosphate-based fertilizers was used as a reference. In the main experiment maize, forage rye, sorghum, and amaranth were cultivated. In the control experiment maize was chosen as the experimental crop again beside sunflower (Table 3-2).

Table 3-2 Cultivated crops and planting density in the pot experiments

Crop species	Variety	Number of plants per pot
Main experiment		
Maize(*Zea mays L.*.)	Fernandez	5
ForageRye (*Hordeum vulgare L.*)	Varda	6
Sorghum (*Sorghum bicolor* Moench)	Zerberus	4
Amaranth(*Amaranthus hypochondracus* L.)	Bärenkraft	5
Control experiment		
Maize(*Zea mays L.*.)	Fernandez	5
Sunflower (*Helianthus annuus L.)*	Rigasol	5

The crops were seeded in April and cultivated for eight weeks. At harvest the crops were in the following growth stages (BBCH): maize 33, sorghum 32, amaranth 51, and rye 30 (Maier et al., 2001). The pots were placed in the greenhouse until germination and afterwards placed in a wire cage in natural weather conditions. Distilled water was used for irrigation and percolated water was collected and replenished. Each treatment consisted of four replicates. At the end of the experiment, plant and soil samples were taken from each pot for laboratory analysis. In the main experiment the effect of fertilizer treatments on P uptake, crop yield as well as on soil pH and soil P pools (sequential extraction) was investigated, while in the control experiment all parameters but the P pools were determined.

3.3.2 Analytical procedure

All fertilizer products were analyzed for total nutrient and heavy metal concentrations using ICP-AES with aqua regia digestion according to DIN EN ISO 15587-1 and DIN EN ISO 17294-2 by the Institute of Conservation and Quality assurance (IUQ). The Pca was determined using citric acid (2%) and a solution: recycled products ratio of 10:1 (VDLUFA, 2007). Oxalate-extractable Fe (Fe_{ox}), Al (Al_{ox}), and P (P_{ox}) in the recycled products were determined by acid ammonium oxalate extraction using a 100:1 oxalate solution to recycled products (Dayton and Basta, 2005). Fe_{ox} and Al_{ox} were not determined in the SSS, because these values are over estimated by the oxalate method in organic rich substrates. The P, Al, and Fe concentrations of the recycled products and TSP were measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES, JobinYvon 238 Ultrace, Instruments S.A. GmbH, D-85630 Grasbrunn) at wavelengths of 214.914 nm (P), 396.152 nm (Al), and 259.940 nm (Fe). To determine the dry-matter yield of the crops, the harvested biomass was dried in an oven at 60 °C and weighed. The P concentration of the grounded plant samples was measured after dry-ashing using the vanadate-molybdate method (Page et al., 1982). The relative P uptake (or effectiveness) (%) of the recycled P products was calculated by comparing the crop P uptake to the P uptake of TSP.

$$\text{Relative effectiveness of recycled products}[\%] = \frac{(\text{P uptake recycled product})}{(\text{P uptake TSP})} * 100$$

The air-dried and sieved (2 mm) soil samples were analyzed for P pools and pH value. The concentrations of bioavailable P (Pdl) was quantified according to Blume et al. (2000). The total P concentration (Pt) was determined after aqua regia digestion by using ICP-OES at a wavelength of 214.914 nm. In addition, soil samples were sequentially extracted according to a modified Hedley procedure (Hedley et al., 1982). In brief, 0.5 g soil was weighed into a 50 ml centrifuge tube.

The soil samples were sequentially extracted for 16 h (each fraction) using an anionic exchange resin, 0.5 M $NaHCO_3$ (pH 8.5), 0.1 M NaOH, and 1 M H_2SO_4 to gain the following P fractions: (1) resin-P (easily exchangeable and soil solution P) (2) $NaHCO_3$-P (labile inorganic and organic P as well as some microbial P), (3) NaOH-P (inorganic and organic P sorbed and/or fixed by Al and Fe oxides minerals and P in humic and fulvic acids), and (4) H_2SO_4–P (associated with Ca and Mg minerals). The P concentration in the supernatant of each fraction was measured using ICP-OES. The residual-P was determined by subtracting the amount of extracted P from the total P content (residual-P = P_t - (resin-P + $NaHCO_3$-P + NaOH-P + H_2SO_4-P). The P inorganic (P_i) concentration in the supernatants of each fraction was determined using the molybdate-blue method (Schinner et al., 1996). The portion of P organic (P_o) was calculated by subtracting Pi of each supernatant from total P concentration of each supernatant. The soil pH was measured in 0.01 M $CaCl_2$ at a soil:solution ratio of 1:2.5 using a pH electrode (Blume et al., 2000). The soil P fractions were analyzed only for the main experiment.

3.3.3 Statistical analysis

Soil and plant data corresponding to four replications were subjected to analysis of variance (General Linear Model (GLM, two-way ANOVA) testing the factor: fertilizer treatment and the factor: crop and interactions of both factors). The results are reported as main and interactive effects. The means of soil and plant parameters were compared by the Tukey test. Significance was determined at $P < 0.05$, and significantly different means were indicated by using different letters.

3.4 RESULTS

3.4.1 Plant biomass and P uptake in dependence of fertilizer treatment applied

Plant characteristics differed considerably between the crops and were affected by the fertilizer treatments (see Table 3-3). Significant interactions between crops and fertilizer treatments indicate that the efficacy of the fertilizer products also depended on the cultivated crop. In the main experiment across all fertilizer treatments the shoot yield ranged as follows: maize > amaranth = sorghum > forage rye (see Table 3-4). In the control experiment the shoot yield of maize was lower than in the main experiment but higher than the shoot yield of sunflower.

Table 3-3 Effect of the fertilizer treatments, crop species and interactions of both factors on shoot yield, P uptake, soil P pools and pH value (p-values).

	shoot	P			Sequential P fractions			
	yield	uptake	Pdl	pH	Resin	$NaHCO_3$	NaOH	H_2SO_4
Main experiment								
Crop species	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000
Treatment	0.000	0.000	0.000	0.006	0.000	0.000	0.000	0.000
Treatment x crop species	0.000	0.000	0.000	0.082^{n}	0.016	0.000	0.000	0.000
Control experiment								
Crop species	0.000	0.001	0.000	0.000				
Treatment	0.000	0.000	0.000	0.001	Not analyzed			
Treatment x crop species	0.000	0.001	0.022	0.002				

Pdl = double lactate soluble P, n.s. = not significant.

Crop P uptake was positively correlated with biomass production, although the correlation was not very pronounced (main experiment r = 0.226**, control experiment r = 0.238*). The P uptake into the shoots of amaranth was considerably higher than the P uptake of the other crops and disproportionately high in relation to the shoot biomass, because of the high P concentration in the plant tissue (see Table 3-5).

Generally, the fertilizer treatments influenced the biomass production less than the crop P uptake. Only for maize (in both experiments) and for sunflower higher shoot yields were measured after P application with the products in comparison to the control. None of the other crops showed higher shoot yields after P application (with the exception of sorghum and rye. after struvite application). Calculating with the average shoot biomass of all cultivated crops, struvite resulted in the highest biomass in both experiments. P addition, however, usually resulted in higher P uptakes in comparison to the control.

On average, the following order of P uptake across all crops could be determined in the main experiment (average P uptakes per pot given in brackets): struvite (149 mg) > 2Mg-SSA (129 mg) > TSP (124 mg) = 1Mg-SSA (123 mg) > 1Ca-SSA (119 mg) = 2Ca-SSA (117 mg) > Al-SSA (112 mg) > Al(ut)- SSA (105 mg) = SSS (105 mg) > CON (95.8 mg).

Table 3-4 Shoot yield of the cultivated crops in pot experiments after application of the amendments and without P addition (CON).

	Main experiment				Control experiment	
	Maize	Sorghum	Amaranth	Foragerye	Maize	Sunflower
	$g\ pot^{-1}$					
CON	53.6 a	44.1 a	47.2 de	25.0 b	48.3 a	41.5 a
	± 5.3	± 2.1	±1.6	±1.1	±3.4	±0.8
SSS	63.8 b	48.3 bcd	46.0 bcd	24.3 ab	48.2 a	42.8 ab
	± 2.3	± 2.0	±0.9	±1.2	±3.4	±1.8
Al(ut)-SSA	64.2 b	49.5 de	45.1 b	23.0 a	60.6 b	45.3 cde
	± 3.5	± 2.3	±0.7	±1.6	±1.7	±1.5
Al-SSA	74.5 c	43.5 a	45.8 bc	23.0 a	62.3 b	45.0 cd
	± 7.4	± 5.2	±1.4	±3.7	±2.7	±0.7
1Ca-SSA	74.5 c	47.1 bcd	46.4 cd	25.3 b	61.7 b	44.3 bc
	± 1.5	± 3.2	±2.3	±0.9	±4.0	±0.9
2Ca-SSA	67.1 b	45.7 ab	47.1 de	25.7 bc	64.5 bc	48.0 f
	± 3.1	± 1.0	±5.1	±1.9	±3.2	±0.6
1Mg-SSA	72.9 c	48.9 cde	48.6 f	25.2 b	68.0 c	46.0 cde
	± 4.7	± 3.8	±0.6	±1.1	±4.4	±0.5
2Mg-SSA	64.1 b	43.6 a	42.6 a	22.6 a	63.9 bc	47.0 ef
	± 3.2	± 2.5	±2.1	±1.9	±2.6	±1.1
Struvite	78.9 d	51.1 e	48.3 ef	27.2 c	64.1 bc	46.6 def
	± 5.6	± 1.7	±3.0	±1.9	±2.1	±0.3
TSP	64.7 b	46.1 abc	47.1 de	25.9 bc	67.8 c	46.5 def
	± 5.7	± 3.3	±0.9	±0.6	±1.3	±1.5
Mean	**67.8 C**	**46.8 B**	**46.4 B**	**24.7 A**	**61.0 B**	**45.3 A**

CON = control treatment, without P addition, SSS = solar dried sewage sludge, SSA = sewage sludge ash, TSP = triple superposphate, ut = untreated, small letters indicate significant differences between the fertilization treatments $P < 0.05$ (Duncan), capital letters indicate significant differences between the crops (separated for each experiment).

The control experiment mostly confirmed this. With the relative effectiveness (%) of the recycled P products the crop P uptake for the treatments was compared with the P uptake after TSP application. In the main and control experiments, the relative effectiveness of the fertilizer treatments ranged as follows: struvite (111–133%), 2Mg-SSA (95–121%), other thermo-chemically treated SSAs (90.4–103%), Al-SSA (88.4–97.8%), Al(ut)-SSA (78–89%), SSS (73.0–92.2%).

Table 3-5 P concentration (Pconc) and P uptake of cultivated crops in pot experiments after application of the amendments and without P addition (CON).

	Main experiment				Control experiment	
	Maize	Sorghum	Amaranth	Foragerye	Maize	Sunflower
P_{conc}	**mg g^{-1}**					
CON	1.52 bc ±0.11	1.61 a ±0.12	3.66 ab ±0.15	2.35 a ±0.15	1.44 ± bc 0.44	1.78 a ±0.05
SSS	1.46 bc ±0.13	1.74 a ±0.22	3.64 a ±0.13	3.06 b ±0.10	1.38 abc ±0.08	1.68 a ±0.16
Al$_{(ut)}$-SSA	1.43 ab ±0.10	1.80 a ±0.03	3.86 abc ±0.25	2.92 b ±0.16	1.32 a ±0.09	1.74 a ±0.15
Al-SSA	1.34 a ±0.14	2.23 bc ±0.29	3.88 bc ±0.10	3.38 de ±0.24	1.44 bc ±0.04	1.94 b ±0.09
1Ca-SSA	1.34 a ±0.06	2.44 bc ±0.31	4.03 c ±0.14	3.10 bc ±0.23	1.38 abc ±0.04	1.98 bc ±0.13
2Ca-SSA	1.55 c ±0.12	2.26 bc ±0.17	3.99 c ±0.25	2.91 b ±0.08	1.34 ab ±0.12	2.13 c ±0.08
1Mg-SSA	1.41 ab ±0.03	2.19 b ±0.21	4.10 cd ±0.03	3.32 cd ±0.19	1.38 abc ±0.04	2.03 bc ±0.12
2Mg-SSA	1.93 d ±0.10	2.83 d ±0.14	4.46 e ±0.69	3.56 e ±0.23	1.55 de ±0.12	2.10 bc ±0.07
Struvite	1.58 c ±0.16	2.97 d ±0.45	4.72 f ±0.21	3.32 cd ±0.44	1.62 e ±0.03	2.53 d ±0.06
TSP	1.57 c ±0.20	2.48 c ±0.20	4.27 de ±0.13	3.14 bc ±0.15	1.48 cd ±0.04	2.11 bc ±0.07
Mean	**1.51 A**	**2.25 B**	**4.06 D**	**3.11 C**	**1.43 A**	**2.00 B**
P uptake	**mg pot^{-1}**					
CON	81.2 a ± 3.7	70.9 a ±4.0	172.8 ab ± 1.9	58.4 a ±4.5	69.4 a ±5.5	73.6 ab ±2.3
SSS	93.5 bc ±10.3	84.0 b ±12.9	167.3 a ± 4.9	74.2 c ±1.9	66.5 a ±6.2	71.6 a ±4.2
Al$_{(ut)}$-SSA	92.0 b ± 3.9	89.0 bc ±7.1	174.0 ab ± 7.8	67.2 b ±1.3	79.8 b ±5.7	78.7 b ±4.8
Al-SSA	99.5 cd ±11.0	97.1 cd ±3.9	177.6 b ± 2.8	77.4 cd ±6.1	89.5 cd ±2.8	87.5 c ±2.6
1Ca-SSA	99.7 cd ± 4.9	114.5 ef ±26.0	186.7 c ± 6.4	78.5 de ±8.8	85.2 bc ±3.4	87.4 c ±4.9
2Ca-SSA	104.1 d ±8.3	103.2 cde ±12.4	187.8 c ±14.1	74.6 c ±3.8	87.6 cd ±4.9	102.0 e ±4.5
1Mg-SSA	102.7 d ±6.2	107.0 ef ±4.06	199.1 d ± 1.7	83.6 f ±1.6	93.8 de ±6.2	93.6 cd ±4.7
2Mg-SSA	123.9 e ±7.5	123.3 g ±7.06	189.9 c ± 5.0	80.5 def ±2.9	99.1 ef ±4.9	98.6 de ±2.3
Struvite	124.7 e ±7.4	151.6 h ±20.9	227.8 e ±14.3	90.0 g ±7.5	104.0 f ±5.1	117.7 f ±2.8
TSP	101.9 d ±7.6	114.2 fg ±7.1	201.2 d ± 7.5	81.2 ef ±5.0	100.0 ef ±1.4	98.2 de ±6.2
Mean	**102.3 B**	**105.5 C**	**188.4 D**	**76.6 A**	**87.4 A**	**90.9 B**

CON = control treatment, without P addition, SSS = solar dried sewage sludge, SSA = sewage sludge ash, TSP = triple superposphate, utuntreated, small letters indicate significant differences between the fertilization treatments P< 0.05 (Duncan), capital letters indicate significant differences between the crops (separated for each experiment).

3.4.2 Bioavailable P and pH values

The Pdl, which represents the P in the soil easily available to plants, and the pH values were affected by the cultivated crops and fertilizer treatments (Table 3-6 and Table 3-7). Again, significant interactions between crops and fertilizer treatments were found. The effect size (partial Eta squared) of the factor fertilizer and the factor crop were similar (0.926 vs. 0.874 in the main experiment, 0.859 vs. 0.921 in the control experiment). The P_{dl} values in the treatments followed a similar order to the P uptakes. Highest values in the main and control experiments were measured for struvite (48.1 and 54.3 mg kg_1soil) and TSP (41.6 and 54.7 mg kg_1soil), whereby after SSS (36.7 and 44.9 mg kg_1soil) and Al(ut)-SSA (36.8 and 47.1 mg kg_1soil) the Pd_l concentrations in the soil were comparably low (averages of all crop treatments).

Table 3-6 Double lactate soluble P (P_{dl}) in soil after addition of the amendments and in the control without P addition (CON) in dependence of the cultivated crops.

	Main experiment				Control experiment	
	Maize	Sorghum	Amarant	Forage rye	Maize	Sunflower
mg kg soil^{-1}						
CON	36.5 a	36.2 a	29.0 a	36.6 a	48.9 a	40.8 a
	±2.0	±1.3	±0.9	±1.0	±1.4	±0.5
SSS	39.9 bc	37.5 ab	31.0 b	38.1 ab	48.9 a	41.0 a
	±0.9	±0.9	±1.1	±0.3	±0.2	±0.3
Al(ut)-SSA	39.0 b	35.8 a	32.9 c	39.6 bc	51.7 b	42.5 de
	±1.6	±1.2	±0.7	±1.4	±0.4	±0.8
Al-SSA	43.6 ef	39.5 cd	39.3 f	43.7 ef	58.0 ef	47.7 b
	±3.0	±1.1	±1.8	±2.0	±0.6	±1.0
1Ca-SSA	41.3 cd	38.8 bc	34.9 d	40.4 cd	54.1 bcd	44.5 c
	±3.1	±0.7	±1.0	±1.0	±0.8	±1.3
2Ca-SSA	39.4 b	38.6 bc	34.2 c	41.9 de	53.3 bc	43.2 b
	±1.9	±2.0	±1.3	±2.1	±2.7	±0.6
1Mg-SSA	40.1 bc	39.9 cd	37.9 ef	44.2 f	56.6 de	47.0 de
	±0.9	±1.0	±2.0	±0.9	±1.3	±0.5
2Mg-SSA	42.9 de	41.0 d	37.0 e	44.2 f	55.0 cd	46.4 d
	±2.0	±1.8	±0.6	±1.7	±2.1	±1.0
Struvite	50.9 g	47.4 e	43.8 g	50.2 g	60.0 fg	49.8 f
	±3.5	±4.6	±3.1	±4.2	±2.8	±0.3
TSP	44.9 f	39.9 cd	36.8 e	44.7 f	61.5 g	48.0 e
	±2.5	±0.9	±1.1	±2.0	±3.0	±1.4
Mean	**41.9 C**	**39.5 B**	**35.7 A**	**42.4 C**	**54.8 B**	**45.1 A**

CON = control treatment, without P addition, SSS = solar dried sewage sludge, SSA = sewage sludge ash, TSP = triple superposphate, ut = untreated, small letters indicate significant differences between the fertilization treatments $P < 0.05$ (Duncan), capital letters indicate significant differences between the crops (separated for each experiment)

The treated SSAs were in between, whereby in both experiments the application of Ca-ashes resulted in lower P_{dl} values in the soil than the Al-SSA and both Mg-SSAs (average of all crop treatments). The P_{dl} concentration of the soil was lowest after the cultivation of amaranth (averages of all fertilizer treatments). The pH in the soil also differed depending on the cultivated crops, with the lowest value found when amaranth (4.5) and sunflower (4.9) were cultivated (average of all fertilizer). Thus, both dicot crops resulted in significantly lower pH values as the monocot crops. Although the fertilizer treatments had a significant effect on pH values, the effect size (partial Eta squared) was considerably lower than the effect size of the crops (0.174 vs. 0.91 in the main experiment, 0.348 vs. 0.91 in the control experiment). Only in combination with amaranth the pH values in the soil increased in the fertilizer treatments in comparison to the control.

Table 3-7 Soil pH values after addition of the amendments and in the control without P addition (CON) in dependence of the cultivated crops.

	Main experiment								Control experiment			
	Maize		Sorghum		Amaranth		Forage rye		Maize		Sunflower	
pH												
CON	5.00 ±0.02	a	5.10 ±0.04	abc	4.37 ±0.05	a	5.18 ±0.05	abc	5.18 ±0.01	bcd	4.85 ±0.06	a
SSS	5.09 ±0.10	a	5.13 ±0.08	bc	4.53 ±0.05	bcd	5.17 ±0.16	abc	5.19 ±0.03	bcd	4.84 ±0.04	a
Al(ut)-SSA	5.17 ±0.04	a	5.15 ±0.04	bc	4.50 ±0.06	bcd	5.29 ±0.03	c	5.20 ±0.04	bcd	4.92 ±0.03	b
Al-SSA	5.08 ±0.45	a	4.99 ±0.07	a	4.41 ±0.11	ab	5.09 ±0.04	a	5.13 ±0.06	abc	4.85 ±0.00	a
1Ca-SSA	4.98 ±0.06	a	5.17 ±0.03	c	4.44 ±0.06	abc	5.19 ±0.03	ab	5.24 ±0.01	d	4.81 ±0.07	a
2Ca-SSA	4.97 ±0.05	a	4.99 ±0.05	a	4.53 ±0.10	bcd	5.14 ±0.04	ab	5.21 ±0.01	cd	4.95 ±0.01	bc
1Mg-SSA	5.00 ±0.02	a	5.14 ±0.14	bc	4.51 ±0.10	bcd	5.26 ±0.15	ab	5.23 ±0.02	d	4.93 ±0.04	b
2Mg-SSA	4.97 ±0.04	a	5.14 ±0.04	bc	4.55 ±0.04	cd	5.14 ±0.08	ab	5.20 ±0.03	Ab	4.92 ±0.02	b
Struvite	5.01 ±0.04	a	5.13 ±0.07	bc	4.50 ±0.07	bcd	5.24 ±0.05	bc	5.08 ±0.13	A	5.00 ±0.02	c
TSP	5.01 ±0.06	a	5.05 ±0.06	ab	4.67 ±0.02	d	5.17 ±0.03	bc	5.12 ±0.06	Ab	4.94 ±0.04	b
Mean	**5.03**	**B**	**5.10**	**C**	**4.50**	**A**	**5.19**	**D**	**5.18**	**B**	**4.90**	**A**

CON = control treatment, without P addition, SSS = solar dried sewage sludge, SSA = sewage sludge ash, TSP = triple superposphate, ut = untreated, small letters indicate significant differences between the fertilization treatments $P < 0.05$ (Duncun), capital letters indicate significant differences between the crops (separated for each experiment).

3.4.3 Soil P fractions

Only in the main experiment was the effect on P fractions analyzed by sequential extraction. The effects of crops and fertilizer treatments as well as their interactions on the P fractions were significant (with the exception of the crop effect on P_t) (Tables 3-8 and 3-9).

Table 3-8 Concentrations of sequentially extracted readily plant available P fractions (percentages of Pt given in brackets) after addition of the amendments and in the control without P addition (CON) in dependence of the cultivated crops.

	Maize			Amaranth			Sorghum			Forage rye		
	mg kg^{-1}	%		mg kg^{-1}	%		mg kg^{-1}	%		mg kg^{-1}	%	
Resin-P												
CON	11.0 ±0.7	(2)	bc	7.8 ±3.2	(2)	a	7.0 ±2.6	(2)	ab	10.2 ±1.1	(2)	b
SSS	7.74 ±1.3	(1)	a	10.5 ±0.8	(2)	bc	8.3 ±0.3	(2)	bc	7.1 ±3.4	(2)	a
Al(ut)-SSA	11.4 ±0.3	(3)	bc	9.6 ±0.4	(2)	ab	5.8 ±1.0	(1)	a	9.1 ±2.6	(2)	ab
Al-SSA	10.1 ±1.3	(2)	b	11.4 ±0.8	(3)	bc	9.8 ±0.8	(2)	bcd	11.2 ±0.9	(3)	bc
1Ca-SSA	11.5 ±0.7	(3)	c	11.3 ±0.6	(3)	bc	9.7 ±0.1	(2)	c	13.5 ±1.7	(3)	cd
2Ca-SSA	13.6 ±0.6	(3)	d	10.7 ±0.4	(2)	bc	12.5 ±0.1	(3)	d	13.6 ±0.9	(3)	cd
1Mg-SSA	11.7 ±1.3	(3)	c	11.2 ±1.7	(3)	bc	9.1 ±0.6	(2)	c	12.2 ±2.9	(3)	bc
2Mg-SSA	14.8 ±0.8	(3)	d	11.9 ±12	(2)	bc	11.8 ±1.6	(3)	cd	14.1 ±2.3	(3)	cd
Struvite	14.1 ±1.2	(3)	d	14.2 ±1.8	(3)	d	12.1 ±1.6	(3)	cd	15.7 ±0.5	(4)	d
TSP	14.0 ±0.6	(3)	d	12.0 ±0.8	(3)	c	9.7 ±1.3	(2)	bcd	13.7 ±1.6	(3)	cd
Mean	**12.0**	**(3)**	**C**	**11.1**	**(2.5)**	**B**	**9.6**	**(2)**	**A**	**12.1**	**(3)**	**C**
$NaHCO_3$-P												
CON	61.3 ±2.4	(14)	a	77.3 ±0.4	(18)	a	55.3 ±4.4	(12)	a	73.5 ±0.6	(17)	b
SSS	65.3 ±8.6	(15)	a	82.1 ±4.8	(18)	ab	65.3 ±8.6	(14)	b	68.0 ±4.2	(15)	a
Al(ut)-SSA	75.8 ±3.7	(17)	b	87.6 ±1.4	(19)	bc	77.5 ±6.7	(17)	c	68.8 ±1.1	(15)	a
Al-SSA	83.2 ±0.3	(18)	cd	94.2 ±2.4	(21)	c	84.1 ±13	(19)	cd	82.5 ±4.4	(18)	cd
1Ca-SSA	79.1 ±5.4	(17)	bc	87.3 ±4.5	(19)	bc	78.4 ±3.6	(17)	c	87.2 ±4.6	(19)	de
2Ca-SSA	77.9 ±5.5	(17)	bc	88.1 ±0.8	(19)	bc	77.9 ±5.5	(17)	c	82.3 ±4.7	(18)	cd
1Mg-SSA	82.9 ±3.5	(19)	cd	88.3 ±1.4	(19)	bc	90.1 ±8.3	(20)	de	81.6 ±3.4	(18)	c
2Mg-SSA	81.4 ±1.1	(18)	cd	93.7 ±12	(18)	c	95.5 ±5.2	(21)	e	94.0 ±1.7	(21)	f
Struvite	86.4 ±1.7	(19)	d	112 ±5.3	(25)	d	91.0 ±6.4	(20)	de	85.2 ±4.3	(19)	cd
TSP	92.8 ±4.8	(21)	e	95.2 ±6.2	(21)	c	90.1 ±2.4	(20)	de	91.6 ±2.4	(20)	ef
Mean	**78.6**	**(17)**	**A**	**90.6**	**(20)**	**C**	**80.5**	**(18)**	**AB**	**81.7**	**(18)**	**B**

CON = control treatment, without P addition, SSS = solar dried sewage sludge, SSA = sewage sludge ash, TSP = triple superposphate, ut = untreated, small letters indicate significant differences between the fertilization treatments $P < 0.05$ (Duncan), capital letters indicate significant differences between the crops.

The NaOH–P fraction (51% of Pt) represented the highest proportion amongst all fractions, followed by H_2SO_4–P (19% of P_t) and $NaHCO_3$–P (17% of Pt) (average values of fertilizer and crop treatments), while resin-P (about 2% of Pt) represented the lowest proportion of all P fractions. Thereby, 30% of $NaHCO_3$–P, 50% of NAOH–P and 10% of H_2SO_4–P were organic P compounds (data not shown), while the proportion of organic P in resin-P was negligible. The resin-P in the soil was lowest after the cultivation of amaranth (average of all fertilizer treatments), which is in relation to the high P uptakes. Interestingly, the $NaHCO_3$ fraction, which is also considered to be highly bioavailable, was not exhausted by amaranth (in contrast to P_{dl} see above). The NaOH-extractable P contents were lowest after sorghum and highest after maize cultivation. The H_2SO_4–P (Ca-P) values were also affected by the crops and decreased the most after amaranth cultivation followed by maize cultivation.

Table 3-9 Concentrations of sequentially extracted less plant available P fractions (percentages of Pt given in brackets) after addition of the amendments and in the control without P addition (CON) in dependence of the cultivated crops.

	Maize		Amaranth		Sorghum		Forage rye	
	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%
NaOH-P								
CON	252 ±2.0	(56) a	218 ±15	(58) a	247 ±14	(55) abc	244 ±8.3	(54) bc
SSS	274 ±5.0	(61) bcd	272 ±5.6	(60) d	254 ±9.8	(56) ab	265 ±4.6	(58) ef
Al(ut)-SSA	300 ±0.9	(66) f	265 ±3.6	(59) cd	235 ±1.3	(52) a	268 ±12	(59) f
Al-SSA	284 ±1.8	(63) e	284 ±1.4	(63) e	260 ±1.8	(58) c	273 ±9.2	(60) g
1Ca-SSA	277 ±3.5	(61) cde	226 ±10	(50) ab	252 ±3.2	(56) bc	259 ±3.4	(57) def
2Ca-SSA	274 ±1.0	(61) bcd	227 ±1.0	(50) ab	242 ±7.7	(54) ab	253 ±1.2	(56) cde
1Mg-SSA	282 ±8.4	(56) de	237 ±8.4	(54) b	252 ±16	(56) bc	238 ±10	(53) ab
2Mg-SSA	268 ±2.7	(59) bc	223 ±2.7	(58) a	253 ±9.3	(59) bc	251 ±5.8	(55) cd
Struvite	268 ±6.3	(59) bc	258 ±8.6	(57) c	249 ±6.1	(55) abc	260 ±3.1	(58) def
TSP	267 ±6.4	(59) b	224 ±3.0	(50) a	252 ±4.4	(56) bc	230 ±13	(51) a
Mean	**274.5**	**(60) C**	**243.2**	**(56) A**	**251.1**	**(56) B**	**254.0**	**(56) B**
H_2SO_4-P								
CON	84.0 ±1.2	(17) a	89.7 ±3.3	(18) a	72.8 ±9.0	(17) a	86.5 ±3.6	(19) Cd
SSS	66.2 ±7.8	(13) a	92.2 ±4.0	(18) a	74.3 ±5.5	(15) a	84.0 ±7.8	(18) Bc
Al(ut)-SSA	112.2 ±7.5	(21) b	99.1 ±0.8	(18) b	88.4 ±5.1	(18) d	91.7 ±0.9	(19) De
Al-SSA	66.5 ±9.5	(13) cd	89.2 ±0.4	(17) a	82.3 ±1.8	(16) bcd	79.6 ±3.1	(17) Ab
1Ca-SSA	94.2 ±5.4	(17) bc	107.6 ±3.1	(22) c	83.8 ±1.8	(18) cd	95.6 ±0.5	(20) Fg
2Ca-SSA	95.3 ±3.1	(17) bc	108.0 ±6.5	(20) c	86.1 ±1.4	(19) cd	103.1 ±1.6	(22) H
1Mg-SSA	103.6 ±4.6	(19) cd	117.2 ±6.5	(20) d	96.7 ±5.5	(21) e	94.9 ±1.8	(20) Ef
2Mg-SSA	81.3 ±5.3	(16) bcd	103.3 ±1.5	(17) bc	75.9 ±0.5	(16) ab	97.4 ±2.0	(19) G
Struvite	59.0 ±6.7	(11) d	91.1 ±2.4	(17) a	81.3 ±2.6	(18) bc	78.2 ±2.6	(16) A
TSP	81.2 ±2.2	(15) e	89.9 ±2.9	(19) a	72.3 ±3.9	(15) a	95.9 ±0.8	(20) Fg
Mean	**84.3**	**(16) A**	**98.7**	**(19) C**	**81.4**	**(17) A**	**90.1**	**(19) B**

CON = control treatment, without P addition, SSS = solar dried sewage sludge, SSA = sewage sludge ash, TSP = triple superposphate, ut = untreated, small letters indicate significant differences between the fertilization treatments $P < 0.05$ (Duncan), capital letters indicate significant differences between the crops.

Application of struvite, 2Mg-SSA, and TSP resulted in the highest concentrations of resin-P and $NaHCO_3$-P in the soil which highlights again the high bioavailability of P in these products. Low values however were found after SSS application. These results are in accordance with the Pdl contents in the soil. The concentration of NaOH-P rose at most after the addition of the Al-SSA and was lowest in the control (275 vs. 240 mg kg^{-1} soil, average after cultivation of all crops). The H_2SO_4-P fraction increased the most after the application of Al(ut)-SSA and the thermo-chemically treated SSA, whereby the lowest P concentration in this fraction was found for struvite, SSS, and Al-SSA. Interactive effects of crops and treatments were found for all fractions (Table 3-3) and the statements made above can partly vary depending on the cultivated crop.

3.5 DISCUSSION

3.5.1 Effects of the P recycled products on crop P uptake and soil P fractions

The results showed that the P nutrition of the crops was strongly affected by the P recycled products. The P fertilizer effect (here we consider the effect on P uptake and the readily soluble P pools) of struvite was found to be similar or even higher than TSP.

As we could find this positive struvite effect for all cultivated crops we assume that this is a valuable P source for a broad spectrum of monocot and dicot crops. The fertilizer effect of recycled products cannot only be explained with the content of P in the product but also with the application of other nutrients as well as with the modification of soil chemistry. Thus, regarding the P_{dl} contents in the soil, struvite resulted in the highest values of all products although the solubility in citric acid was lower than for TSP. The high P_{dl} values are even more remarkable since the P uptake of crops fertilized with struvite exceeded those of the other treatments, which in turn should have exhausted the P_{dl} pool. Relatively low P solubility in citric acid was also found for 2 Mg-SSA, however, this product resulted together with TSP and struvite in the highest P concentrations of the readily available resin and $NaHCO_3$ fraction (averages of all crop treatments). This showed that the effectiveness of recycled P products is not always well indicated by their solubility in water or 2% citric acid and may rather depend on their dissolution in the soil (Cabeza et al., 2011). Positive effects can be related to Mg incorporated with struvite and its synergistic effect on P uptake Römer (2006) and Gonzalez-Ponce et al. (2009). This is also relevant for the Mg-SSAs (see below). The treated SSAs had a relatively high P fertilizer effect which was in the range of TSP, or even surpassed TSP as was the case for 2Mg-SSA for the most analyzed parameters. The high solubility of many Mg phosphates can partly explain the superiority of Mg-SSAs to Ca–P and Al–P based recycled products. Thermo-chemically treated Mg-SSAs and Ca-SSAs contain P associated with Ca; however the Ca-SSAs can contain higher concentrations of hardly soluble Ca–P compounds and have a higher crystallinity compared to Mg-SSAs (Nanzer at al., 2014b; Adam et al., 2009 Adam et al., 2009). Vogel et al. (2013) highlighted the different reactions of Ca-and Mg-pyrophosphate in the soil, whereby mainly Mg-pyrophosphate formed plant-available P phases. According to Römer (2006) is the P availability from primary, secondary, and tertiary Mg phosphates similar to that of primary Ca phosphate. In our study we could prove the relatively high bioavailability of Mg phosphates by higher P concentrations in the readily bioavailable P pools (P_{dl}, resin-P, and $NaHCO_3$) after application of Mg-SSAs (mainly 2Mg- SSA) than after application of Ca-SSAs and Al-SSA. The P fertilizer effect of 1Mg-SSA and 1Ca-SSA was usually lower than 2Mg-SSA and 2Ca-SSA which might be related to the lower P concentration in the first ashes. To warrant the P application of 200 mg per pot, larger quantities of ash needed to be applied, which also resulted in the greater application of Al, Fe, and Ca and thus probably in higher P sorption in the soil or the formation of less available P compounds. The soil pH values for ash treatments were almost the same, so the soil reaction cannot explain the different effects on soil P pools. The lower crop P uptake of Al-SSA compared to Mg-SSA and Ca- SSA can be explained by the high concentration of oxalate-soluble Al (mainly considered as amorphous Al or Al-oxides/hydroxides) in the Al-SSA (see Table 3-1) as H_2SO_4 digestion increases not only the solubility of P in Al-based SSA, but also the concentration of amorphous Al (Petzet et al., 2012). Amorphous Al, however, can increase the P sorption capacity in the soil (O'Connor et al., 2004; Agyin-Birikorang et al., 2007). In this context we found highest values of the NaOH-P fraction – which is considered as a P pool associated to amorphous Fe and Al – for the Al-SSA treatment followed by the other Al-based products. The Ca-SSA and Mg-SSA also contained Al and Fe but in a less amorphous form, since the H_2SO_4 digestion was not completed as in the case of Al-SSA and the oxalate soluble Al and Fe concentrations were lower than for the Al-SSA and Al(ut)-SSA. Thus, despite the high total Fe concentra- tion of 1Ca-SSA, the NaOH-P pool was rather low after application of this product, probably because of the predominant crystalline structure of Fe. This is supported by the study of Nanzer et al. (2014a), where even an increase in the crystallinity of Fe compounds was observed after thermo-chemical treatment. Therefore, it must be considered that particularly a long-term application of treated Al-SSA can increase the concentration in amorphous Al in the soil and therefore the P sorption capacity in the soil.

In addition, amorphous Al is toxic to plants in high concentrations (see Chapter 4.2). The average P uptake of the cultivated crops and the P concentration in the bioavailable P pools (resin, $NaHCO_3$, Pdl) were higher after Al(ut)-SSA application than for the control, but lower compared to the treated SSA. The low P solubility of untreated SSA is related to the high concentration of hardly soluble P compounds (Peplinsky, 2009; Nanzer et al., 2014a). The direct comparison of Al(ut)-SSA with Al-SSA showed that a chemical treatment of the SSA by the H_2SO_4 digestion led to an increased P-availability for the crops. Finally, the SSS application had usually the lowest P fertilizer effects of all products which rarely surpass the control. High amounts of Al and Fe applied with the SSS (see Table 3-1), which has likely increased the sorption capacity in the soil, and hardly soluble P forms in the sludge are probably the reasons for these results. In a longer-term study a better effect might be found, due to the transformation of hardly soluble P compounds into better available forms in the soil (Krogstad et al., 2005).

3.5.2 Crop effects and correlation between crop and soil characteristics

The P fertilizer effects of the P products applied were quite comparable in both experiments. However, some products reacted differently in combination with certain crops, which was also shown by the significant interactive effects in the GLM analysis and indicated that the efficacy of the fertilizer products can also depend on the cultivated crop. For example, when Al-SSA was applied to maize higher yields and P uptakes were measured in comparison to the control. When Al-SSA was applied to amaranth, however, the P uptakes were comparable to those found in the control and even lower yields were measured. For amaranth low yields were found when relatively high amounts of Al were applied with the products, which was true for Al-SSA, Al(ut)-SSA, and SSS. This can be explained by the low pH values after amaranth cultivation (4.4 in the Al-SSA treatment), which likely resulted in a toxic effect of the released Al. Al toxicity mainly occurs at low pH and results in a reduction of crop yields (Chen et al., 2012). An increased risk of Al toxicity was even observed when pH values were below 5.2 (Oladeji et al., 2009). The low pH value after amaranth cultivation could also have been the reason for the low P concentration in the H_2SO_4 fraction, which is associated with Ca and Mg minerals. Differences in the efficacy of recycled products depending on the cultivated crops were also found previously with biomass ashes applied to eight different crops in a pot experiment (Schiemenz and Eichler-Löbermann, 2010). Generally, the yield effects of the fertilizer treatments were lower than the effects on P uptake. This relatively small effect of P supply on yields may indicate that the amount of P in the soil (despite suboptimal P_{dl} content in the treatment without fertilization) was still sufficient to meet plant demand. Even P compounds with relatively low solubility can be mobilized in the soil by crops and microorganisms, and such processes might not be reflected adequately by standard soil-P extraction methods (Requejo and Eichler-Löbermann, 2014;

Dakora and Phillips, 2002; Eichler- Löbermann et al., 2007). Besides the bio-chemical mobilization, the internal P utilization efficiency varies between crop plants, and plants which produce a greater yield per unit of P can be considered to have a high internal P utilization efficiency (Lambers et al., 2010). Considering the high P concentration in the shoot tissue of amaranth the internal P utilization was rather low. However, the high P uptake of this crop suggested a high efficiency for P acquisition (see below). In our experiments relatively low P concentrations were found in maize biomass. Intraspecific comparisons, however, showed evidence of variation in internal P use between cultivars of one species (Akhtar et al., 2008), and here we can only make predictions for the cultivars tested in our experiment. The P concentration in the plant-available P pools is affected by the P uptake of the crops. Thus, including all crops in the calculation, a negative correlation (0.289*, n = 160) between P uptake and P_{dl} values was found indicating lower soil P values with higher P uptakes of the crops (such as for amaranth). However, as on average more P was applied than the plant took up the P supply with the fertilizers resulted in both higher P_{dl} concentrations and higher plant P uptakes. Following, P_{dl} and P uptake were positively correlated when considering the plants separately (ranging from 0.698** for maize to 0.875** for sorghum, n = 40). Close positive correlations were also found between P uptake of the individual crops and the P concentration in the resin and $NaHCO_3$ fractions which were also significant at $p < 0.01$ level. Amaranth was the crop with the highest P uptake, which partly overcame the amount of P applied with the fertilizers. And here we only consider the shoot P uptake, because we did not investigate the P uptake into the roots. The high P uptake of amaranth was in relation to the relatively low concentration of readily available P pools (see also above). The lowest pH values in the soil probably occurred because of the release of organic acids. This was shown by Li et al. (2006), who cultivated amaranth under K stress. We assume that in our experiment the amaranth roots released organic acids to mobilize P resources in the soil and to cover the high P demand of this crop. Only for amaranth did the application of the P fertilizers partly result in an increase of pH values in comparison to the control. Extremely high P uptakes by amaranth were also found in other studies (Escudero et al., 1999; Ojo et al., 2010; Brandt et al., 2011; Bachmann et al., 2011). Higher yields of maize in the main experiment than in the control experiment can be explained with the lower temperatures in 2012 in comparison to 2011. The average temperature in April was 10.1°C in 2011 and only 7.6°C in 2012 (DWD, Groß Lüsewitz). Also in May and June the temperatures in 2011 were higher than in 2012 (DWD, 2011, 2012).

3.6 Conclusions

The utilization of P recycled products as fertilizer is an important strategy to create nutrient cycles in agriculture and to save nutrient resources. Struvite as well as treated SSAs can be considered as effective sources for P fertilization on acidic loamy sands. Generally, these products increased the P uptake of different crops and the readily plant available P pools in the soil in comparison to the control to a similar extent as TSP. The 2Mg-SSA was shown to have a better effect on various characteristics (P uptake and readily available soil P pools) than the other SSAs. Thus, for thermo-chemical treatment the use of a Mg donor (as $MgCl_2$) should be preferred. The results of this study highlighted especially the fertilizer effect of struvite independently of the cultivated crop. The application of Al-SSAs on acid soils is less recommendable, because of the high concentration of oxalate-soluble Al in the products and the enrichment of P in the NaOH fraction in the soil. Interactive effects of recycled products and cultivated crops on soil P fractions should be considered in the nutrient management for crops. The crop effects need further consideration and the P utilization from wastewater products should be investigated with different crops under field conditions to verify the results obtained under semi-controlled conditions. Considering all soil and crops data we could give the following ranking for the products: Struvite > Mg-SSAs > Ca-SSAs, Al-SSAs > SSS.

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4 PHOSPHOR EFFECTS OF RECYCLED PRODUCTS FROM MUNICIPAL WASTEWATER ON CROPS IN A FIELD EXPERIMENT

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4.1 ABSTRACT

In this study, the P fertilizing effect of struvite, one thermo-chemical-treated sewage sludge ash based on Ca-P (Ca-SSA) and one full sulfuric acid digested SSA based on Al-P (Al-SSA) was analysed in comparison to triple superphosphate (TSP) and a control treatment (CON) without P application in a two-year field experiment. In the field experiment, the effects of the recycled products on crop yield, P uptake and labile soil P fractions were analysed. In addition, the effect of nitrogen and magnesium contained in struvite was investigated in the second year of the experiment compared to TSP and CON. In the first year, spring barley was cultivated in the field experiment; and in the second year, it was forage rye followed by sorghum. In the second year the relative P effectiveness (forage rye, sorghum) of the recycled products compared to TSP increased in the order Ca-SSA (81%, 91%) ≤ Al-SSA (91%, 96%) = struvite (102%, 110%). In addition, a magnesium fertilizing effect of struvite could be demonstrated. The results showed that the recycledproducts from wastewater treatment are appropriate to substitute rock phosphate based fertilizers.

4.2 INTRODUCTION

Currently, mainly phosphate rock (PR)-based fertilizers are used in agriculture, but the majority of the PR resources are possessed by only a few countries and are enriched with cadmium and uranium (Jasinski, 2014). Therefore, phosphorus (P) recycled from waste products for food production is the primary concern to guarantee the security of supply in Europe (Elser et al., 2014). Municipal wastewater is, in addition to manure, one of the most important P sources as it contains 16% of the mined P (Cordell et al., 2009). The direct use of sewage sludge, a residue of wastewater treatment, is declining in some EU member states since sewage sludge entails the risk to contain critical amounts of organic contaminants and heavy metals. For instance, Germany restricted the use of sewage sludge to smaller wastewater treatment plants (capacity in relation to population equivalent < 50 000) and Switzerland banned the direct application of sewage sludge (Kabbe et al., 2015). Therefore, technologies to recycle P from wastewater treatment are in development (Sartorius et al., 2012). Among these recycled products, struvite ($MgNH_4PO_4 \cdot 6\ H_2O$) is of particular significance due to its low concentration in contaminants and its high P availability, which was in the range of highly water soluble P fertilizers (Rahman et al., 2014). However, only a maximum of 40% of P in wastewater inlet can be recovered by struvite precipitation (Kabbe et al., 2015). Higher loads (up to 90%) of P from wastewater treatment can be recovered by mono incineration of sewage sludge (sewage sludge ash, SSA) combined with subsequent chemical treatment (Sartorius et al., 2012). The chemical treatment of SSAs is required to increase the P bioavailability and to achieve the legal limit values for heavy metals. The P fractions in treated SSAs vary considerably according to the used precipitating agent during the whole P recycled process and include readily soluble P and P adsorbed and precipitated on Al-, Fe-, Mg- and Ca-compounds (Donatello and Cheesman, 2013).

In several pot experiments, a higher P availability of struvite compared to treated SSAs for diverse crops was observed, which was in the range of rock phosphate-based fertilizers (Severin et al., 2013, Vogel et al., 2015). Fewer efforts have been made to evaluate the P availability of struvite and SSAs for crops in the field. Pot experiments are necessary to produce replicable and comparable data, but their results cannot extrapolate to the field since pot conditions are very different from field conditions (e.g. soil temperature, aeration, water content) (Passioura, 2006). This highlights the role of field experiments.

In general, the focus of research has been on the P fertilizing effect of struvite, while the research regarding the effect of magnesium (Mg: 10%) and nitrogen (N: 6%) in struvite on crop growth has been less pronounced (Bonvin et al., 2015). Mg is of particular importance, as Mg contents in cereal seeds have declined over the last decades (Cakmak, 2013).

Therefore, the objectives of the present study were (1) to investigate the P fertilizing effect of struvite and SSAs under natural conditions in a field experiment in relation to their main P-binding forms and (2) to investigate the N and Mg fertilizing effect of struvite. It is hypothesized that the P fertilizing effect of these recycled products is adequate for plant nutrition in the field and that struvite can promote crop growth by its magnesium and nitrogen fertilizing effects.

4.3 MATERIALS AND METHODS

4.3.1 Characteristics of fertilizer treatments

The recycled products differed in composition in relation to the recycling process and raw material used (Table 1). The used struvite was produced according to a process developed by the Berliner Wasserbetriebe (BWB), where the digested sludge is aerated in a reactor to raise the pH up to 8 for struvite precipitation by stripping CO_2 and adding $MgCl_2$ (Kern et al., 2008). Two treated sewage sludge ashes were tested (the nomenclature was done according to the main P binding form in the ashes). For Al-SSA, P was precipitated in the wastewater with Al before the sludge was mono incinerated. The ash was then treated by a H_2SO_4-washing procedure and 300 g H_2SO_4 (96%) per kg SSA was added to increase the P availability. More detailed information of the process is available in Petzet et al. (2011). The Ca-SSA was thermo-chemically treated, whereby heavy metals were evaporated in a rotary furnace at a temperature of 1000°C after the addition of $CaCl_2$ (Ca-SSA) as a chlorine donor at a rate of 100 mg/kg ash. Afterwards, 30% H_2SO_4 was added to increase the P availability. A more detailed description of the process can be found in Adam et al. (2009). The same recycled products were used in a previous incubation experiment and in a previous pot experiment carried out by Vogel et al. (2015, 2017). Highly water soluble triple superphosphate (TSP) was used as a reference.

Table 4-1 Application rate (kg/ ha), total P (P_t) content and solubility of P (Citric acid soluble P, P_{ca}) (g/kg), total nutrient concentration (K, Mg, Ca, N, Al, Fe) (g/kg dry matter) as well as the pH of the recycled products and TSP (Vogel et al. 2017)

	Rate	P_t	P_{ca}	K	Mg	Ca	N	Al	Fe	pH
	(kg/ha)	(g/kg dry matter)								
Al-SSA	854.7	58.5	45.9	5.1	7.7	42.6	n.d.	55.8	10.4	1.9
Ca-SSA	1126.1	44.4	29.1	4.4	15.0	96.1	n.d.	26.2	54.5	3.9
Struvite	410.8	121.7	102.7	0.6	93.4	4.9	41.7	39.6	18.5	7.5
TSP	318.5	157.0	168.9	n.d.	8.9	106.7	n.d.	29.4	22.5	2.3

SSA: sewage sludge ashes; n.d.: not determined.

4.3.2 Experimental design and soil characterization

In 2010 and 2011, a field experiment was carried out at the experimental station of the University of Rostock, which is located in Mecklenburg-Vorpommern (MV) in northeast Germany. Soil was low acidic (pH 5.8) loamy sand (Stagnic Cambisol) with total P (P_t)

content of about 515 mg/kg. The double lactate soluble P (P_{dl}) and Mg (Mg_{dl}) content in soil averaged at P_{dl}: 55 mg/kg and Mgdl: 114 mg/kg, indicating a suboptimal P supply (category B) and a high Mg supply (category E) (Schweder et al., 2004). In the field experiment, treatments with struvite, Al-SSA, Ca-SSA, TSP and a treatment without P application (CON) were carried out in three repetitions. The crops were cultivated on plots with the size of 4.5 × 6 m or 4.5 × 4.5 m in three repetitions. Edge effects were eliminated by harvesting only the centre of the plots (3 × 1.5 m). In the first year spring barley and in the second year forage rye (catch crop) followed by sorghum (main crop) were cultivated (Table 2). The surface biomass was harvested by cutting the plants within the measurement area.

In the field experiment, 50 kg P_t/ha was inserted into the soil in 2010 for the complete experimental time. N and K were applied in the experiment uniformly by mineral fertilizer. During the first year 110 kg N/ha and 80 kg K/ha and during the second year 140 kg N/ha and 110 kg K/ha were added by commercial fertilizers. Mg was not applied by mineral fertilizer since the Mg concentration in soil was at a level that further yield increase was no longer possible by applying more Mg. In addition, nutrients were supplied in different amounts by the recycled products and TSP. Soil samples were collected before fertilizer application, after the harvest of spring barley and in the second year after the harvest of the main crop (sorghum) at 0–30 cm depth in order to determine the effect of labile P pools. The effects of N and Mg contained in struvite on crop yield and P availability were investigated in comparison to TSP and CON only in the second year of the field experiment.

Table 4-2 Cultivated crops, variation of crops and seed rate in the field experiments.

Crop	Cultivar	Seed rate	Sowing time	Time of harvest
Spring barley *(Hordeum vulgare L.)*	Marthe	300 g.s./ m²	08.04.2010	10.08.2010
Forage rye (*Secale cereal L.*)	Varda	140 kg/ ha	01.10.2010	11.05.2011
Sorghum (*Sorghum bicolor* Moench)	Zerberus	25 g.s./m²	20.05.2011	30.09.2011

g.s.: germinable seeds

4.3.3 Chemical analysis

To determine the dry matter (DM) yield of the crops, the harvested biomass was dried in an oven at 60°C for seven days and then weighed. The P and Mg concentration of the ground plant samples was measured after dry ashing using the vanadate-molybdate method (Page et al. 1982) and the N content was determined after wet digestion of the ground plant material using the Kjeldahl apparatus. The relative P effectiveness (RPE) (%) of the recycled products was calculated by comparing their P uptake to the P uptake of TSP.

$$\text{RPE of the recycled products [\%]} = \frac{(\text{P uptake recycled product})}{(\text{P uptake TSP})} * 100$$

Air-dried and sieved (2 mm) soil samples were analysed for double lactate extractable P using the method described by Blume et al. (2000). The water-extractable P (Pw) was determined by extracting the soil samples with distilled water with a soil:water ratio of 1:25 (Van der Paauw 1971).

4.3.4 Statistics

Statistical analysis was performed with the software package PASW Statistics 18 (SPSS, Hong Kong, Ltd.). Analysis of variance (ANOVA, general linear model) was followed by a Duncan’s multiple range test at the 0.05 level of significance to compare the means of soil and plant parameters.

4.4 RESULTS AND DISCUSSION

4.4.1 First year of the field experiment

In the first year of the field experiment, the rain was much lower in April (44%) as well as in June (46%) and July (81%) compared to the average values of the years 1991 to 2010, while at harvest time (August) the rain was twice as high as the average values of the years 1991 to 2010 (Figure 4-1).

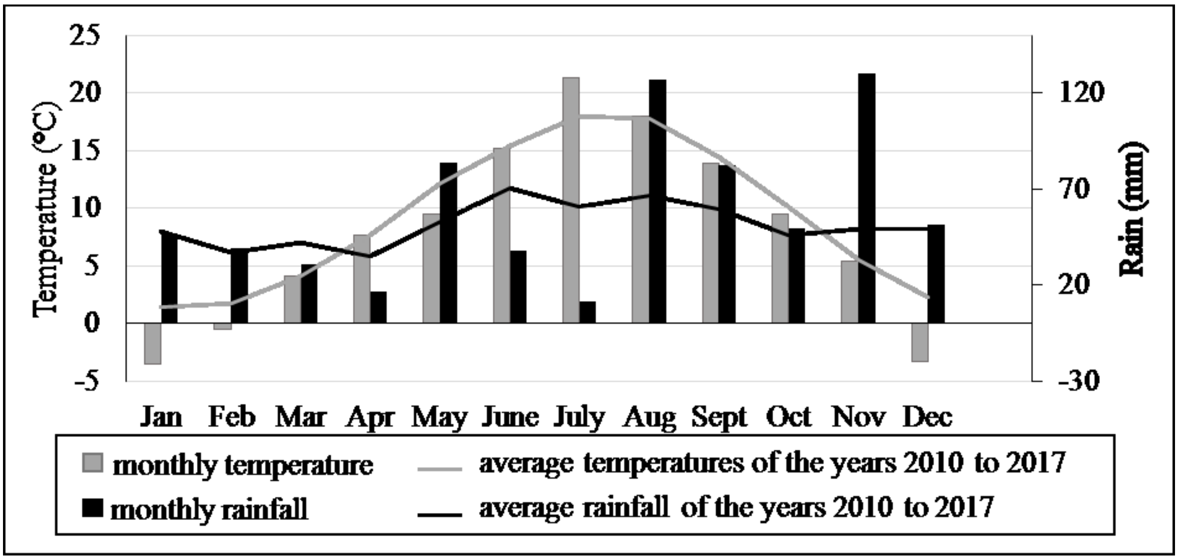

Figure 4-1 Monthly temperature and monthly rainfall of 2010 for Rostock; the values were compared to the average values of the years 1971-2010 (mean) for Rostock (Deutscher Wetterdienst)

The temperature in 2010 was in the range of the average values of the years 1971 to 2010. As a consequence, the dry matter yield of spring barley in the field experiment was rather low due to the dry July and the wet August in 2010. In the field experiment, no increases of P uptake and yield of spring barley by the recycled products and TSP compared to CON were observed (Tabel 4-3). Concerning the low yield, this low effect on yield is most likely due to the soil P concentration in the field experiments, which was adequate for spring barley. A stronger effect of the P treatments on labile P fractions was found. Pdl in soil was increased by 34% to 46% after application of struvite and TSP compared to CON, whereas the Pdl value in soil was not increased after application of the Al-SSA and the Ca-SSA compared to CON. In addition, the Pw concentration in soil was increased by struvite (by 22%) and by TSP (by 21%) compared to CON, while no effect of the Ca-SSA and the Al-SSA on Pw compared to CON was observed.

Table 4-3 Dry matter (DM) yield, phosphorus (P) uptake of spring barley as well as double lactate soluble P (P_{dl}) and water soluble P (P_w) concentration in soil after addition of recycled products, triple super phosphate (TSP) and control treatment without P addition (CON) in the first year after cultivation of spring barley.

	DM yield	P uptake	P_{dl}	P_w
	(t/ha)	(kg/ha)	(g/kg soil)	
spring barley				
CON	3.7 ±0.27 a	10.8 ±3.4 A	51.9 ±6.5 a	16.6 ±2.1 a
Struvite	4.0 ±0.30 a	13.9 ±1.6 A	69.7 ±3.2 b	20.2 ±0.4 b
TSP	4.1 ±0.14 a	14.8 ±4.1 A	76.0 ±1.0 b	20.0 ±1.4 b
Al-SSA	4.3 ±0.10 a	11.6 ±0.8 A	60.7 ±1.8 a	15.4 ±1.8 a
Ca-SSA	4.4 ±0.24 a	11.8 ±0.7 A	58.0 ±0.6 a	16.4 ±1.2 a

SSA: sewage sludge ashes. Small letters indicate significant different means between fertilizater treatments. Duncan's test a > 0.05; ± the standard error of the means.

The lower effect of the Ca-SSA on labile soil P pools (P_{dl}, P_w) compared to struvite can be explained by different reaction mechanisms of Mg-P and Ca-P in soil. Over time, Mg-P reacts in soil to the plant available trimagnesium phosphate, while Ca-P converts to the plant unavailable hydroxyapatite (Vogel et al., 2013). In addition, the chlorine donor ($CaCl_2$) used during thermo-chemical treatment of the Ca-SSA resulted in the formation of poor soluble P compounds, which were not completely decomposed by the partial H_2SO_4 treatment (Nanzer et al., 2014). This was visible in the low concentration of citric acid soluble P (plant-available proportions of P_t) of the Ca-SSA (Table 4-1). The lower P effect on labile soil P pools of the Al-SSA compared to struvite can be related to its high concentration of amorphous Al (54.2 g/kg) since Al-rich P recycled products reduced the bioavailability of P in the first months after application to acidic soils due to the increase of P sorption capacity

(Bøen et al. 2013). This effect of the Al-SSA on the P sorption capacity in acidic soil was demonstrated in a previous incubation experiment (Vogel et al., 2017). In addition, it is assumed that the nitrification of NH_4 contained in struvite further enhanced its P solubility compared to the SSAs in soil by decreasing the soil pH near the struvite crystals since P dissolution of struvite is thought to increase under acidic conditions (Achat et al., 2014). This is confirmed by Daumer et al. (2007), who demonstrated that the dissolution of struvite increased during the treatment of piggery wastewater due to the fall in pH near the nitrifying bacterial floc by the release of H^+ ions.

4.4.2 Second year of the field experiment

In 2011, there was too dry spring with lower rain levels in February (31%), March (61%) and April (30%) compared to the average values of 1971 to 2010, while the level of rain in June (44%), July (81%) and August (46%) was much higher compared to the average values (Figure 4-2). The temperature was again in the same range compared to the average values of 1971 to 2010.

In 2011, the yield of forage rye was in the lower range of values that can be achieved in Mecklenburg-Vorpommern and can be related to the drought from February to April (Figure 4-2).

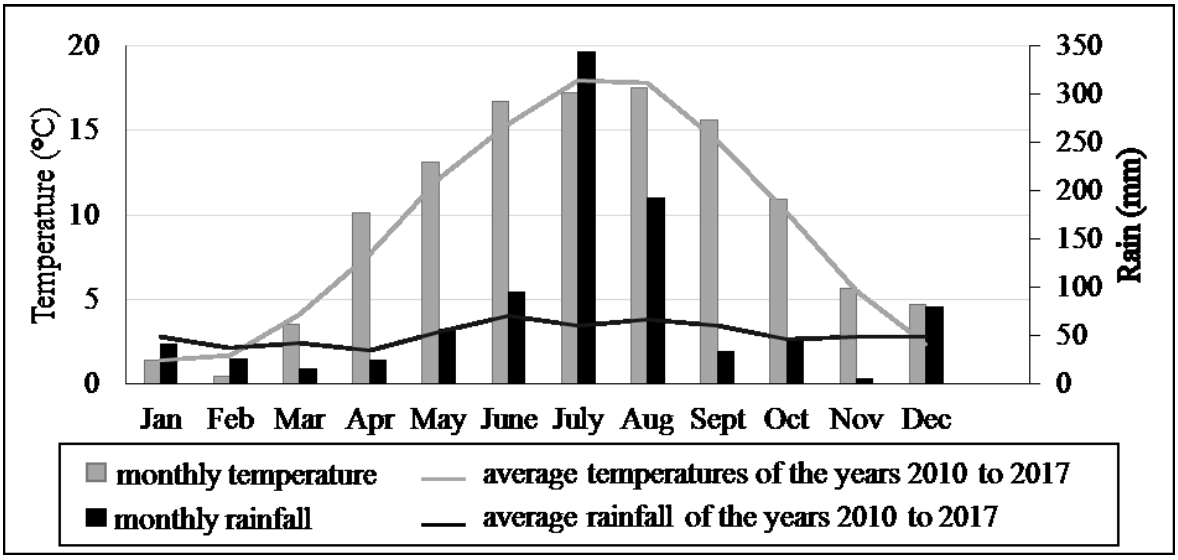

Figure 4-2 Monthly temperature and monthly rainfall in 2011 for Rostock; the values were compared to the average values of the years 1971–2010 (mean) for Rostock (Deutscher Wetterdienst)

The dry matter yield of forage rye was increased by struvite (by 36%), the Al-SSA (by 21%) and TSP (by 33%) compared to CON, while the Ca-SSA had no effect on the dry matter yield of forage rye compared to CON (Table 4-4). The P effectiveness of struvite (102%) and the Al-SSA (91%) after cultivation of forage rye was in the same range compared to TSP, while the P effectiveness of the Ca-SSA (81%) was lower compared to TSP. This can be explained by the dissolution behavior of the Ca-SSA in soil and its concentration of low soluble P compounds, as described above. The yield of sorghum in the field experiments was rather low since in north Germany the cultivation of sorghum imposes generally late sowing due to the relatively low temperatures in spring (Ercoli et al., 2004). In this field experiment the yield (by 32% to 44%) and P uptake (by 33% to 50%) of sorghum were increased by the recycled products and TSP compared to CON (Taable 4-4).

The yield and P uptake after application of the SSAs and struvite were in the same range compared to TSP. This can be illustrated by the P effectiveness of the recycled products compared to TSP after cultivation of sorghum, which increased in the same order as after the cultivation of forage rye: Ca-SSA (91%) ≤ Al-SSA (96%) ≤ struvite (110%).

Table 4-4 Dry matter (DM) yield, phosphorus (P) uptake of cultivated crops as well as double lactate soluble P (Pdl) and water soluble P (Pw) concentration in soil after addition of recycled products, triple superphosphate (TSP) and control treatment without P addition (CON) in the second year after cultivation of forage rye and sorghum.

	DM yield			P uptake			Pdl			Pw		
	(t/ha)			(kg/ha)			(g/kg soil)					
forage rye (catch crop)												
CON	3.3	±0.2	a	7.3	±1.0	a	n.d.			n.d.		
Struvite	4.1	±0.3	b	9.9	±0.8	b	n.d.			n.d.		
TSP	4.2	±0.3	b	9.7	±1.1	b	n.d.			n.d.		
Al-SSA	3.8	±0.4	ab	8.8	±0.9	b	n.d.			n.d.		
Ca-SSA	3.3	±0.4	a	7.9	±1.3	a	n.d.			n.d.		
sorghum (main crop)												
CON	8.1	±0.9	a	17.1	±0.7	a	47.2	±8.8	a	12.7	±1.4	a
Struvite	11.1	±1.4	b	25.6	±2.9	c	66.4	±11.2	a	17.3	±1.8	b
TSP	11.3	±1.2	b	23.3	±1.2	bc	63.3	±4.8	a	16.6	±1.0	b
Al-SSA	10.8	±0.8	b	22.4	±2.8	bc	57.5	±2.8	a	11.3	±1.8	a
Ca-SSA	11.0	±0.6	b	21.2	±0.7	b	56.8	±4.8	a	13.0	±1.0	a

SSA: sewage sludge ashes. Small letters indicate significant different means between fertilizater treatments. Duncan's test a > 0.05; ± the standard error of the means.

After the cultivation of forage rye followed by sorghum no differences between the Pdl concentration in soil of the P fertilizer treatments and the CON treatment were observed, while Pw in soil was higher in the TSP treatment (by 39%) and in the struvite treatment (by 32%) compared to CON. This indicates again that struvite has higher P bioavailability than the Al-SSA and the Ca-SSA. However, the high P effect of the Ca-SSA on the yield of sorghum is in contrast to their effect on the yield of forage rye, which was lower compared to TSP. It cannot be fully clarified with our study, why sorghum and forage rye showed different yield responses to the fertilizer treatments, but the rapidly growing root system of sorghum may have increased soil exploitation and consequently the P supply in the Ca-SSA-treatment (Khalili et al., 2008).

The high effectiveness of P contained in the Al-SSA found in the field experiment for forage rye and sorghum is in contrast to the results of a previous pot experiment (over eight weeks), where a lower P uptake in the Al-SSA treatment compared to TSP after cultivation of forage rye and sorghum was found in acidic soil (pH 5.2) (Vogel et al., 2015). As described above, the low P availability for crops found in the pot experiment can be related to its effect on P sorption capacity in the first month after addition to acidic soils. However, Al-P contained in soil after the first growing season is thought to be available to plants in the coming growth season (e.g. Krogstad et al., 2005), which was confirmed by this field experiment.

In addition, it must be considered that the SSAs have to be applied in higher amounts to the soil compared to struvite due to their lower P concentrations. This might increase the risk of heavy metal accumulation in soil still further, in particular since the SSAs contain higher amounts of heavy metals compared to struvite (Vogel et al., 2017). Furthermore, struvite precipitating is already implemented and operating in full scale, while the processes for recovering P from mono incinerated SSA are currently tested in a pilot phase and the whole P recovery process including the mono incineration and the post-treatment of the SSA is a cost and energy-extensive process (Kabbe et al., 2015).

The fertilizing effect of struvite and TSP on N and Mg uptake was only analysed during the second year after cultivation of forage rye and sorghum. The N uptake was increased by struvite and TSP compared to CON after cultivation of sorghum (Table 4-5). This can be attributed to the P-fertilizing effect of struvite and TSP (Achat et al., 2014), which increased the yield and consequently the N uptake of sorghum as described above. Concerning the low initial N dose applied by struvite (17.1 kg/ha) and the N supply by commercial fertilizer, no N fertilizing effect of struvite could be demonstrated. The Mg uptake of forage rye and sorghum was increased by struvite compared to CON and TSP (Table 4-5), which can be related to the Mg dose applied by struvite (38.4 kg/ha). This is confirmed by González-Ponce et al. (2009), who observed a higher Mg uptake by lettuce after struvite application compared to single superphosphate.

Table 4-5 Nitrogen (N) and magnesium (Mg) uptake of (kg/ha) cultivated crops after addition of struvite and triple superphosphate (TSP) and control treatment without phosphorus (P) addition (CON) in the second year after cultivation of forage rye and sorghum

	N uptake (kg/ha)			Mg uptake (kg/ha)		
forage rye (catch crop)						
CON	38.8	±6.3	a	3.14	±0.2	a
Struvite	43.1	±3.9	a	3.82	±0.3	b
TSP	44.5	±5.4	a	3.34	±0.2	a
sorghum (main crop)						
CON	72.3	±7.3	a	17.4	±4.0	a
Struvite	103.0	±5.4	b	26.6	±3.8	b
TSP	102.3	±3.0	b	18.7	±1.2	a

SSA: sewage sludge ashes, small letters indicate significantly different means between fertilizer treatments. Duncan's test a > 0.05; ± the standard error of the means

4.5 CONCLUSION

In conclusion, P contained in the recycled products studied here was readily available for the cultivated crops in the acidic soil under field conditions, and consequently these recycled products can reduce the dependence on rock phosphate-based fertilizer. The results in the first year of the field experiment indicate that the bioavailability of struvite is higher compared to the Ca-SSA and the Al-SSA. In addition, the Mg fertilizing effect of struvite found in this field experiment showed that struvite can contribute to an increase of the Mg-concentration in food crops. In case of the Al-SSA, its P availability is likely too low for crops in the first growing season, and therefore needs to be applied in combination with highly water soluble P fertilizer. However, possible negative effects of these recycled products on crop growth need to be excluded in further pot experiments and in long-term field experiments (e.g. Al toxic effects on crops) and under diverse soil conditions.

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5 GENERAL DISCUSSION

In this chapter, the findings of chapter 2 to 4 are jointly discussed in order to enable a conclusive and comprehensive assessment of the fertilizer quality of the recycled products from wastewater treatment studied here and to derive conclusions for future research. In addition, the findings are discussed in the context of of the current technical, logistical, economical and legal conditions in Germany to assess the possibility of introducing these recycled products into the German market.

5.1 P FERTILIZING EFFECT OF RECYCLED PRODUCTS FROM WASTEWATER TREATMENT

The recycled products from wastewater differed in their P speciation and metal concentration (Al, Fe, Ca, Mg) and consequently in their dissolution behavior in soil as well as in their P bioavailability, which were investigated in one incubation experiment, two pot experiments and one two-year field experiment. The results of the pot experiments showed that the effectiveness of the recycled products increased in relation to TSP in the order SSS (73-92%) = Al(ut)-SSA < treated SSAs (88-121%) < struvite (111-131%). This indicates, that P recycling from wastewater treatment in form of struvite and treated SSA not only reduce the level of contamination compared to sewage sludge, but also have a positive effect on the P bioavailability. In the pot experiments, the lowest P uptake by cultivated crops was found in the SSS-treatment compared to the other P fertilizer treatments, which can be related to the respective concentration in Fe and Al of the SSS. This most likely increased the P sorption capacity in the acidic soil, which applies to the most sewage sludges as mainly $FeCl_3$ or $Al_2(SO_4)_3$ are currently used for P precipitating during wastewater treatment (Donatello and Cheeseman, 2013). In addition, the results of the experiments confirmed the results of previous studies, that a chemical treatment of SSAs is usually necessary to increase the P bioavailability of mono incinerated sewage sludge (e.g. Krüger and Adam, 2015; Nancer et al., 2014a). Among the tested SSAs, the untreated SSA (Al(ut)-SSA) represents the highest concentration of P compared to the treated SSAs, but showed the lowest P solubility in soil (incubation experiment, Chapter 2) and the lowest P availability for the cultivated crops in the pot experiments (Chapter 3). This can be related to its high concentration in crystalline Ca-P (Chapter 2), which play only a minor role for the P nutrition of crops (Akhtar et al., 2009). In addition, the results of the incubation experiment showed, that the Al(ut)-SSA increased the P-sorption capacity in the acidic soil due to its high concentration in amorphous

Al and Fe (Chapter 2). However, the results of the pot experiments showed, that the P bioavailability of the treated SSAs was in the range of TSP. The treated SSAs differed in their P solution kinetic in soil (Chapter 2) and in their P bioavailability (Chapter 3, Chapter 4) due to their different concentration of nutrients and metals. These differences in elemental composition can be explained by differences in the origin as well as by production processes and subsequent chemical treatments. In the pot experiments the P effectiveness of the treated SSAs increased in relation to TSP in the order: Al-SSA (88-98%) = Ca-SSAs (94-103%) ≤ Mg-SSAs (94-121%). The highest P effectiveness was found for the Mg-SSAs, which can be related (1) to their lower concentration in crystalline Ca-P compared to the Ca-SSAs, (2) to their lower concentration of amorphous Al and Fe compared to the Al-SSA and (3) to their P dissolution kinetic in soil. Mg-P is regarded to react in soil to the plant available trimagnesium phosphate, while Ca-P converts over time to hydroxyapatite, which is unavailable to the plant. (Vogel et al., 2013; Römer, 2006). The higher concentration in amorphous Al and Fe of the Al-SSA compared to the Mg-SSAs (Chapter 2) increased the P sorption capacity in the acidic soil in the first month after application (Bøen et al., 2013). This increase in P sorption capacity after application of the Al-SSA was demonstrated in the incubation experiment (Chapter 2) and by its effect on the NaOH-P fraction (P chemisorbed to Fe and Al) in the main pot experiment (Chapter 3, Figure 5-1). However, Al-P contained in soil after the first growing season is thought to be available to plants in the coming growth season (e.g. Krogstad et al., 2005), which was confirmed by this field experiment. Nevertheless, the P bioavailability of the Al-SSA is likely too low for crops in the first growth season, and therefore needs to be applied in combination with highly water-soluble P-fertilizer. In addition, the application of Al rich SSA is questionable, because Al is considered to inhibit root growth and consequently the acquisition of nutrients in strongly acidic soils (Delhaize and Ryan, 1995; Kochian et al. 2004). On the other hand, the application of the amorphous Al rich Al-SSA on high P saturated soils can contribute to reduced eutrophication by P losses in surface waters due to the removal of dissolved P from agricultural runoff water (e.g. Dayton and Basta, 2005). However, the Mg-SSAs showed not only a higher P bioavailability compared to the Al-SSA but Mg-P is also known to be less influenced by soil pH also compared to Ca-P (Achat et al., 2014). The P bioavailability of Ca-P highly decreased in alkaline soils (Warren et al. 2009). Consequently, the Mg-SSA can most likely be used in a wider range of soil pH compared to the Al-SSA and Ca-SSA.

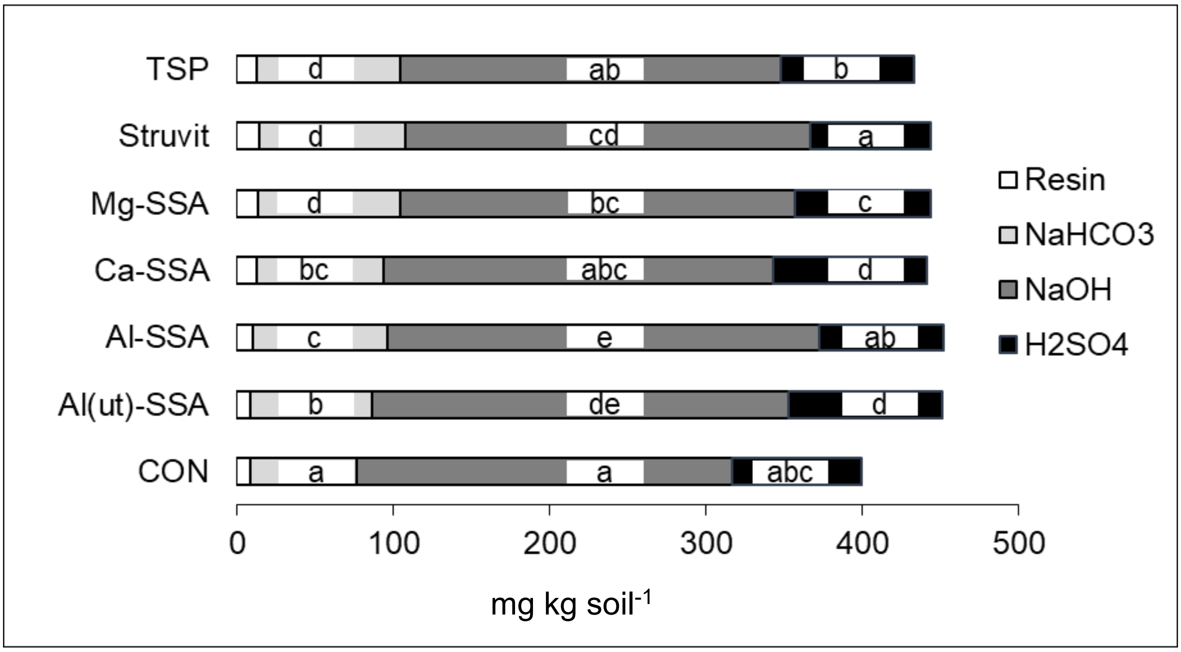

Figure 5-1 Concentrations of sequentially extracted P fractions after addition of the amendments and in the control without P addition (CON) averaged for all cultivated crops in the main pot experiment.

Among the recycled products, the highest P bioavailability was observed for struvite. The P effect of struvite on readily plant available P fractions in soil found in all experiments (Chapter 2, Chapter 3, Chapter 4, Figure 5-1) was in the range of TSP and so was its P bioavailability found in both pot experiments and in the field experiment. This high P bioavailability of struvite can be related to the acidic soil conditions, which increased the initial P dissolution rate of struvite in soil (Bhuiyan et al., 2007; Massey et al., 2009; Talboys et al., 2016). Another reason for the high P availability is the enhanced decrease in soil pH next to the struvite granules by nitrification of the ammonia contained in struvite, which probably further favored the P dissolution of struvite. This is confirmed by Daumer et al. (2007), who demonstrated, that the dissolution of struvite increased during the treatment of piggery wastewater due to the fall in the soil pH near the nitrifying bacterial floc by release of H^+ ions. The decreasing effect of struvite on soil pH was demonstrated after three days of incubation in the incubation experiment. In addition, the high P effectiveness of struvite can be explained by the different reaction mechanisms of Mg-P and Ca-P in soil as described above (Vogel et al., 2013). Moreover, the results of the field experiments indicate, that the yield of cultivated crops was supported by the Mg-fertilizing-effect since the Mg-uptake in the field experiment was increased by struvite compared to TSP and CON (chapter 4). However, struvite might increase P loss to surface or groundwater in particular when applied in large quantities to highly P saturated acidic soils.

5.2 DIFFERENT EFFECTS OF CROP SPECIES ON THE P AVAILABILITY OF RECYCLED PRODUCTS

In the pot experiments, significant interactions between crops and fertilizer treatments were found, which indicate that the efficacy of the fertilizer products also depended on the cultivated crop. In this work, the different effects of the C_3- and C_4-species and of monocots and dicots on the P bioavailability of the recycled products were estimated. While no differences were found in P use efficiency between C_3- and C_4-species, the P use efficiency was increased by dicots compared to monocots. This result is confirmed by the results of Halsted and Lynch (1996) and Taleboys et al. (2016), who found a significant higher effect of dicots by organic acid exudation on the P bioavailability of P fertilizers compared to monocots. Nevertheless, it must be considered that in this study the investigation concerning the P acquisition mechanism on P uptake was only possible to a limited extent since e.g. mechanism concerning altered root morphology and architecture could not be examined in the pot experiments due to the limited soil volume in the pots. However, in the main pot experiment the dicot crop (amaranth, pH: 4.5) increased the P solubility more compared to the monocot crops (forage rye, maize, sorghum; pH: 5.0 to 5.2) most likely due to the strongly decreased soil pH after cultivation of amaranth (Chapter 3). This decrease in soil pH after cultivation of amaranth resulted in a two to threefold higher P uptake of amaranth compared to the monocot crops (chapter 3). The decrease in soil pH after cultivation of dicot crops was confirmed in the second pot experiment after cultivation of sun flower (dicot, pH: 4.9) compared to maize (monocot, pH: 5.2). However, the results of the pot experiments indicate that crops can promote the P bioavailability of all recycled products in soil studied here, but does not change the order in which the P bioavailability of the recycled products from wastewater decreased in respect to their P speciation: struvite ≥ Mg-SSA ≥ Ca-SSA = Al-SSA.

5.3 RISK ASSESSMENT OF HEAVY METAL ACCUMULATION AND USE OF RECYCLED PRODUCTS FROM WASTEWATER TREATMENT IN GERMANY

In case of the SSA, the risk of contamination with organic contaminants can be almost entirely excluded as organic contaminants get destroyed during incineration, but the SSA contains critical amounts of heavy metals (Krüger and Adam, 2015). The studied untreated SSA (Al(ut)-SSA) cannot be used as fertilizer in Germany due to its degree of contamination, which for Pb, Ni and Hg are not within the limits of the German fertilizer ordinance (DüMV).

The heavy metal concentration of the treated SSAs varied considerably due to used recycling process and raw material. Among the thermo-chemical treated SSAs, the heavy metal concentration is generally higher in $MgCl_2$ treated SSAs compared to the $CaCl_2$ treated SSAs (Chapter 2), which is confirmed by Nancer et al. 2014b. However, the Al-SSA contain higher loads of Pb, Zn and Cu compared to the thermo-chemical treated SSAs, while the thermo-chemical treated SSAs contain higher concentrations of Ni. These heavy metals are essential nutrients in low concentrations, but toxic to plants in relatively high concentrations (Miraglia et al., 2009; Sreekanth et al., 2013). Struvite is certified as safe fertilizer, which in the case of heavy metals is confirmed by the results of this thesis. However, struvite contains organic contaminants and heavy metals, albeit in very low concentrations (Kern et al., 2008). In fact, struvite contains the lowest level of heavy metals compared to the other recycled products from wastewater treatment and contains even lower amounts of As and Cd compared to TSP. The same is true for the treated SSAs in respect to the Cd concentration compared to TSP (Chapter 2). Therefore, the continuous usage of rock phosphate based P fertilizers holds the risk of Cd accumulation in soil and plant tissue as Cd can readily be taken up by plants, because of its high mobility (McLaughlin and Singh, 1999; Uraguchi et al., 2009). The future use of P fertilizer based on newly found, highly Cd contaminated phosphate rock (PR) deposits further exacerbates the risk of Cd entering into the human food chain (von Horn and Satorius, 2009). Therefore, the use of rock phosphate based P fertilizer should be avoided. An increasing use of struvite and the SSAs as fertilizer in agriculture can contribute to minimize the use of rock phosphate based P fertilizer in the next years.

Over the next few years, it can be expected that struvite precipitation processes will be implemented at least in the wastewater treatment plants with enhanced biological phosphorus removal. In Germany, 1,300 t P a^{-1} could already be recycled by struvite precipitation under optimum conditions and consequently struvite will become more relevant for use as P fertilizer in agriculture (Montag et al., 2015; Kabbe et al. 2015).

Currently about 12% of the annual consumed rock phosphate based P fertilizer in Germany (150.000 t P a^{-1}) can be replaced by the mono incinerated SSAs (19,000 t P^{-1}), but it must be considered that these SSAs mostly needs to be further treated to reduce their heavy metal concentration and to increase their P bioavailability. In Germany, no facility for P recovery from SSAs works at full scale, but the development of P recycling processes from SSAs are in progress and will be implemented in full scale in the coming years (Kabbe et al., 2015).

5.4 OVERALL CONCLUSION AND FUTURE RESEARCH DIRECTIONS

This study demonstrates the need to analyze the P fertilizer effectiveness of the recycled products from wastewater treatment comprehensively. The defining of the chemical composition and the observation of the incubation study were of great importance for explaining the P availability of the recycled products for plants in the pot experiments and in the field experiment. In addition, this study highlights the importance to analyze the P availability for plants not only in pot experiments but also in multiyear field experiments. For instance, the high P availability of the Al-SSA for plants in the second growth season found in the field experiment could not be demonstrated in the pot experiments due to the limited experimental time.

The results of this thesis demonstrate a high P fertilizing effect of struvite and the treated SSAs, which was comparable to TSP in the used acidic soil. Whereby, these results showed that Mg-P based recycled products from wastewater, in particular of struvite, are more efficient P fertilizer than the Ca-SSAs and the Al-SSA. This indicates, that Mg based agents to recover P from SSAs should be preferred over Ca and Al based P precipitation agents in respect to the P bioavailability of the recycled products. In addition, struvite and likely also the Mg-SSAs can contribute to the reduction of present-day Mg-deficiency in food crops. Since the results of the field experiment showed that the Mg uptake was increased by struvite, this most likely also applies to the Mg-SSAs.

However, struvite is not only the most P efficient fertilizer, but also the most ecologically friendly P fertilizer among the recycled products of wastewater treatment. Since struvite contains far lower concentration of heavy metals compared to the SSAs and even lower concentrations of Cd and As than TSP. Consquently, struvite can decrease the accumulation of Cd in the soil-plant system compared to TSP, which is considered to be associated with severe human health problems when entering the food chain. The here studied SSAs contain also lower Cd concentration than rock phosphate based P fertilizers, but it must be considered that the SSAs can increase the input of other heavy metals (e.g. Zn, Ni, Pb) into the soil-plant-system.

In summary, struvite precipitating should be favored in terms of its higher P bioavailability, its lower impurities and its economic viability compared to SSAs, but the P recovery rate of struvite is much lower than that of SSAs (Table 5-1) (Montag et al., 2015). Therefore, after the present conditions of the technical and operational possibilities struvite precipitating and

P recovery from SSA are necessary for a sustainable P recovery from the wastewater stream (Krüger et al., 2016).

Table 5-1 General characteristic of struvite and mono incinerated sewage sludge ash.

	Struvite	Treated SSA
P recovery potential	10 - 40%*	70 - 90%*
Mean P concentration	12%**	2-12%***
P availability for crops	++	+
Heavy metals	--**	-***
Organic contaminants	--**	--***
Costs	-	+
State of maturity	Full scale	Pilot phase
Future relevance	++	++

* Montag et al., 2015, values refer to the P concentration in the total waste water treatment plant inlet in Germany (65.897 t P* y^{-1}). ** Rahman et al., 2014, Kern et al, 2008. *** Krüger and Adam, 2015, +: high, –: low.

Although many questions concerning the fertilizer quality of recycled products from wastewater treatment have been answered in this thesis, a number of issues have not yet been investigated sufficiently.

The major factors determining the P concentration in soil solution are the soil pH and the concentrations of metals (Ca, Fe and Al) (e.g. Hinsinger, 2001). Therefore, it is of high importance to analyze the P fertilizing effect of the recycled products from wastewater treatments also under neutral to alkaline soil conditions. The concentrations of Al, Fe, Ca and/or Mg contained in the recycled products are determined by the P precipitation agent that was used during the P recycling processes (Donatello and Cheeseman, 2013). These metals can have adverse effects on crop growth (e.g. Reduction of the bioavailability of nutrients, toxic effects on crops) (Hinsinger, 2001; Kochian et al., 2004; Kataki et al., 2016). Therefore, the investigation of the effect of these metals in long term field experiments is necessary in order to to exclude adverse effects on the soil-plant-system and to make recommendations regarding the future use of agents for P recovering during wastewater treatment and the subsequent recycling of P. In addition, the P dissolution kinetics of the recycled products in soil and their P bioavailability needs to be analyzed in more detail by labeling the P contained in the recycled products from wastewater treatment, for example by radioisotope approach to be able to differentiate between P derived from the soil and P derived from the fertilizer. In particular, the dissolution behavior of struvite is not yet understood. For instance, struvite has a slower solubility in neutral extractants (e.g. distilled water), but is highly soluble in neutral soils (e.g. Bonvin et al., 2015). This indicates that the

P solubility of struvite is supported by other soil characteristics and/or microbial species (e.g. by nitrification). Therefore, it is of significant importance to determine how the P bioavailability of the recycled products from wastewater treatment is influenced by soil characteristics and/or microbial species. In addition, the results of the pot experiment showed that the P bioavailability of the recycled products is influenced by cultivated crops. This highlights the need to analyze the effect of different acquisition mechanism of diverse crops on the P bioavailability of recycled products in more detail in pot- and long term field experiments. Moreover, long term field experiments are of significant importance to determine the risk of the accumulation of contaminants in soil and their uptake by crops and to rule out adverse effects of the recycled product of wastewater treatment on the soil-plant-system and human health.

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6 APPENDIX

Supplemental Table 6-1 Effect of the recycled products and triple superphosphate (TSP) on the soil pH after 1, 3, 7, 14, 35, and 70 days of incubation.

Treatment	Days					
	1	3	7	14	35	70
CON	5.66 f^{C} ±0.02	5.52 e^{A} ±0.01	5.55 f^{B} ±0.00	5.54 d^{B} ±0.02	5.55 e^{B} ±0.00	5.54 e^{B} ±0.01
Al-(ut)SSA	5.34 b^{A} ±0.07	5.48 d^{B} ±0.01	5.53 e^{B} ±0.02	5.62 e^{C} ±0.01	5.66 f^{CD} ±0.01	5.68 f^{D} ±0.02
Al-SSA	4.06 a^{B} ±0.04	3.93 a^{A} ±0.02	3.96 a^{A} ±0.01	4.19 a^{C} ±0.01	4.15 a^{C} ±0.02	4.18 a^{C} ±0.01
1Ca-SSA	5.52 e^{C} ±0.03	5.53 e^{C} ±0.01	5.46 d^{B} ±0.01	5.45 c^{B} ±0.01	5.42 bc^{A} ±0.02	5.43 c^{A} ±0.01
2Ca-SSA	5.42 cd^{C} ±0.02	5.35 b^{B} ±0.02	5.29 b^{A} ±0.01	5.42 b^{C} ±0.02	5.41 b^{C} ±0.01	5.40 b^{C} ±0.01
1Mg-SSA	5.48 de^{A} ±0.07	6.04 g^{E} ±0.03	5.92 g^{D} ±0.00	5.83 f^{C} ±0.00	5.77 g^{B} ±0.01	5.73 g^{B} ±0.00
2Mg-SSA	5.47 cde^{C} ±0.02	5.43 c^{B} ±0.01	5.38 c^{A} ±0.02	5.45 c^{BC} ±0.02	5.44 c^{B} ±0.01	5.46 d^{BC} ±0.02
struvite	6.22 g^{B} ±0.02	6.65 h^{F} ± 0.01	6.54 h^{E} ±0.03	6.47 g^{D} ±0.01	6.26 h^{C} ±0.02	6.15 h^{A} ±0.03
TSP	5.40 bc^{A} ±0.03	5.59 f^{D} ± 0.03	5.47 d^{B} ±0.02	5.53 d^{C} ±0.01	5.47 d^{B} ±0.02	5.43 cd^{AB} ±0.02

CON: control treatment (without P application); SSA: sewage sludge ash, TSP: triple superphosphate, ut: untreated, small letters indicate significant differences between the fertilization treatments, within a column; capital letters indicate significant differences between the times of incubation within a line; P< 0.05 (Duncan)

Supplemental Table 6-2 Effect of the sewage sludge products and triple superphosphate (TSP) on water soluble phosphorus (Pw) and double lactate soluble phosphorus (Pdl) in soil after 1, 3, 7, 14, 35, and 70 days of incubation.

	days											
Treatment	1		3		7		14		35		70	
Pw (g kg^{-1})												
CON	15.3 ±0.36	a^{D}	13.7 ±0.18	a^{BC}	12.9 ±0.12	a^{A}	13.2 ±0.75	a^{AB}	14.0 ±0.19	a^{C}	13.4 ±0.28	a^{ABC}
Al(ut)-SSA	15.0 ±0.67	a^{B}	16.2 ±0.28	a^{C}	14.2 ±0.52	a^{A}	14.5 ±0.11	a^{AB}	16.0 ±0.18	a^{C}	16.0 ±0.11	a^{C}
Al-SSA	38.0 ±1.86	b^{DE}	39.4 ±1.68	b^{E}	34.7 ±2.48	b^{CD}	29.1 ±4.06	b^{AB}	31.1 ±1.02	b^{B}	26.3 ±1.56	ab^{A}
1Ca-SSA	39.6 ±1.75	b^{A}	40.5 ±2.23	b^{A}	38.2 ±2.02	b^{A}	37.7 ±3.85	b^{A}	39.6 ±4.71	c^{A}	34.9 ±1.74	b^{A}
2Ca-SSA	67.9 ±3.54	c^{C}	66.3 ±0.87	c^{C}	55.7 ±2.75	c^{AB}	60.0 ±1.88	c^{B}	52.3 ±3.16	d^{A}	51.3 ±1.19	c^{A}
1Mg-SSA	66.0 ±1.27	c^{BC}	72.1 ±7.83	c^{C}	55.5 ±3.06	c^{A}	59.3 ±9.35	c^{AB}	59.9 ±3.33	d^{AB}	58.8 ±1.96	c^{AB}
2Mg-SSA	120.6 ±4.86	d^{D}	123.0 ±3.66	d^{D}	110.3 ±8.67	d^{C}	107.2 ±4.92	d^{BC}	99.3 ±4.27	e^{AB}	96.7 ±5.51	d^{A}
struvite	126.6 ±0.55	e^{B}	136.7 ±3.61	e^{B}	128.6 ±0.87	e^{B}	98.6 ±16.0	d^{A}	134.7 ±12.2	f^{B}	124.2 ±20.7	e^{B}
TSP	154.4 ±1.46	f^{C}	163.6 ±5.18	f^{D}	143.4 ±6.21	f^{B}	149.0 ±1.98	e^{BC}	129.8 ±5.01	f^{A}	131.1 ±5.42	e^{A}
Pdl (g kg^{-1})												
CON	50.6 ±3.43	a^{A}	50.0 ±1.44	a^{A}	51.4 ±0.62	a^{A}	52.7 ±1.30	a^{AB}	55.9 ±3.77	a^{B}	49.3 ±1.62	a^{A}
Al-(ut)SSA	73.3 ±1.87	b^{A}	75.7 ±4.37	b^{AB}	74.5 ±5.10	b^{AB}	83.0 ±5.79	b^{BC}	81.6 ±1.12	b^{ABC}	89.1 ±6.39	b^{C}
Al-SSA	188.3 ±2.18	e^{C}	182.4 ±2.16	e^{B}	180.2 ±3.20	e^{B}	188.6 ±4.99	e^{C}	173.9 ±2.54	e^{A}	208.6 ±0.93	d^{D}
1Ca-SSA	96.5 ±1.57	c^{A}	99.2 ±2.18	c^{A}	108.8 ±1.87	c^{B}	108.6 ±8.04	c^{B}	96.5 ±1.10	c^{A}	96.4 ±7.42	b^{A}
2Ca-SSA	136.9 ±4.84	d^{C}	136.9 ±14.7	d^{C}	146.5 ±12.3	d^{D}	131.0 ±1.30	d^{B}	137.9 ±16.5	d^{C}	118.0 ±0.35	c^{A}
1Mg-SSA	190.3 ±8.02	e^{A}	193.4 ±9.36	f^{A}	183.6 ±8.73	e^{A}	186.3 ±7.49	e^{A}	198.8 ±7.94	f^{A}	223.4 ±12.6	e^{B}
2Mg-SSA	236.4 ±5.66	f^{AB}	246.0 ±13.2	g^{B}	223.5 ±6.24	f^{A}	221.5 ±0.72	f^{A}	233.1 ±5.16	g^{AB}	250.2 ±14.7	f^{B}
struvite	317.1 ±1.25	h^{B}	377.3 ±2.18	i^{C}	371.3 ±4.37	h^{C}	312.1 ±6.24	h^{B}	308.4 ±16.5	i^{B}	264.1 ±2.20	g^{A}
TSP	270.3 ±6.60	g^{B}	299.9 ±5.44	h^{C}	259.7 ±7.48	g^{AB}	266.2 ±13.6	g^{AB}	260.0 ±13.6	h^{AB}	247.9 ±7.87	f^{A}

CON: control treatment (without P application); SSA: sewage sludge ash, TSP: triple superphosphate, ut: untreated, small letters indicate significant differences between the fertilization treatments, within a column; capital letters indicate significant differences between the times of incubation within a line; $P < 0.05$ (Duncan)

Supplemental Table 6-3 Effect of the recycled products and triple superphosphate (TSP) on the degree of P saturation (DPS) and P sorption capacity of the soil (PSC) after 1, 7, 35 and 70 days of incubation.

Treatment	Days			
	1	7	35	70
DPS(%)				
CON	45.0 a^{AB} ±0.51	43.3 a^{A} ±3.46	48.8 a^{C} ±3.00	42.7 a^{A} ±2.71
Al-(ut)SSA	65.8 b^{C} ±1.17	58.4 b^{A} ±4.26	63.8 b^{BC} ±0.47	64.3 b^{BC} ±3.54
Al-SSA	67.6 b^{AB} ±4.85	63.0 c^{A} ±4.03	66.1 b^{AB} ±18.2	66.3 b^{AB} ±8.28
1Ca-SSA	84.6 ef^{A} ±3.02	80.9 ef^{A} ±2.97	82.3 c^{A} ±5.96	82.9 cd^{A} ±2.67
2Ca-SSA	73.1 bcd^{A} ±5.45	73.8 d^{A} ±2.12	79.4 c^{A} ±6.84	77.3 c^{A} ±2.61
1Mg-SSA	82.2 cde^{B} ±4.00	76.3 de^{A} ±3.70	77.4 c^{A} ±1.06	78.3 c^{AB} ±4.61
2Mg-SSA	70.8 bc^{A} ±3.39	77.6 de^{B} ±0.37	76.8 c^{B} ±1.34	75.9 c^{B} ±4.56
struvite	93.9 f^{A} ±6.27	104.1 g^{B} ±5.34	92.4 d^{A} ±9.40	88.3 d^{A} ±7.64
TSP	82.5 de^{A} ±9.12	84.1 f^{AB} ±1.19	82.1 c^{AB} ±4.51	85.9 d^{B} ±4.26
PSC (mmol kg^{-1})				
CON	26.2 a^{AB} ±0.84	25.8 a^{A} ±1.20	26.2 ab^{AB} ±0.20	27.6 a^{A} ±1.17
Al-(ut)SSA	28.8 b^{A} ±1.19	29.5 bc^{B} ±1.45	32.5 c^{B} ±3.07	28.2 a^{A} ±1.50
Al-SSA	36.5 c^{B} ±1.12	36.4 d^{B} ±0.36	31.1 bc^{A} ±4.84	33.2 b^{A} ±2.88
1Ca-SSA	26.2 a^{A} ±0.14	26.1 a^{A} ±0.88	26.1 ab^{A} ±1.46	26.1 a^{A} ±0.94
2Ca-SSA	27.5 ab^{A} ±0.58	27.5 ab^{A} ±0.17	26.2 bc^{A} ±1.69	26.4 a^{A} ±1.22
1Mg-SSA	26.7 a^{A} ±1.43	27.2 ab^{A} ±2.72	26.4 ab^{A} ±1.19	27.1 a^{A} ±1.22
2Mg-SSA	28.7 b^{A} ±0.51	29.9 c^{A} ±1.77	28.2 d^{A} ±0.15	28.1 a^{A} ±0.77
struvite	26.1 a^{A} ±1.54	25.0 a^{A} ±2.45	25.6 a^{A} ±1.95	26.6 a^{A} ±0.78
TSP	26.7 a^{A} ±0.54	27.4 ab^{B} ±0.41	27.5 bc^{B} ±0.53	28.4 a^{B} ±1.07

CON: control treatment (without P application); SSA: sewage sludge ash, TSP: triple superphosphate, ut: untreated, small letters indicate significant differences between the fertilization treatments, within a column; capital letters indicate significant differences between the times of incubation within a line; $P < 0.05$ (Duncan)

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8 PROOF OF INDIVIDUAL CONTRIBUTION

Manuscript including in the thesis	**Author**	**Co-Author**
Telse Vogel, Jens Kruse, Nina Siebers, Michael Nelles, Bettina Eichler-Löbermann: *Recycled products from municipal wastewater: Composition and effects on phosphorus mobility in a sandy soil.* **Journal of Environmental Quality,** (2017). 46, pp. 443-451. **Chapter 2**	Generating research idea, generating and evaluating data, writing the manuscript.	Jens Kruse (correcting the manuscript) Nina Siebers (generating research idea, correcting the manuscript) Michael Nelles (correcting the manuscript) Bettina Eichler Löbermann (correcting the manuscript)
Telse Vogel, Michael Nelles, Bettina Eichler-Löbermann: *Phosphorus application with recycled products from municipal wastewater to different crop species.* **Ecological Engineering,** (2015), 83, pp. 466-475. **Chapter 3**	Generating research idea, generating and evaluating data, writing the manuscript	Michael Nelles (correcting the manuscript) Bettina Eichler Löbermann (correcting the manuscript, generating research idea)
Telse Vogel, Michael Nelles, Bettina Eichler-Löbermann: *Phosphor effects of recycled products from municipal wastewater on crops in a field experiment.* **Environment, Plant and Soil** Received: 27.07.2017 **Chapter 4**	Generating research idea, generating and evaluating data, writing the manuscript	Michael Nelles (correcting the manuscript) Bettina Eichler Löbermann (correcting the manuscript, generating research idea)

9 THESES

Phosphor effects of recycled products from wastewater treatment on the soil-plant-system

Presented by Telse Vogel

I Objectives of research

Phosphor (P) is an essential nutrient and thus indispensable for food production. Currently, mainly phosphate rock (PR) based fertilizers are used in agriculture, but global PR reserves are limited. In addition, PR deposits contain substantial concentrations of contaminants such as Cd, which can be taken up by crops and thus can increase the risk of Cd transfer to the food chain. Therefore, P recycling from waste products for food production is a primary concern for maintaining food security for a continuously growing world population.

Municipal wastewater is an important source to recover P as it contains up to 16% P of the input of mined PR, but wastewater is often rich in heavy metals and organic contaminants. Therefore, several new processes to recover P during wastewater treatment or from byproducts of wastewater treatment (e.g. sewage sludge) were developed during the past years to decrease the level of contamination. The resulting products differ in P speciation, P solubility and in nutrient and heavy metal concentration due to the raw material and used P recovery process that were used. Therefore, these new P recycled products from wastewater have to be evaluated carefully in order to ensure an adequate P supply for crops and to avoid adverse effects on the soil-plant-system and human health.

In this thesis, the P fertilizer quality of promising recycled products from wastewater treatment was investigated comprehensively. These recycled products from wastewater treatment differed in their main P binding form due to the used recycling process and raw material and include struvite, one solar dried sewage sludge based on Fe-P, one untreated (ut) sewage sludge ash (SSA) based on Al-P (Al(ut)-SSA), one total H_2SO_4-digested SSA based on Al-P (Al-SSA), and four thermo-chemically treated SSAs (two Mg-SSAs and two Ca-SSAs).

In order to assess the future significance of these recycled products from wastewater treatment to replace PR based fertilizers their P fertilizer quality was investigated in regard to (1) their composition with the focus on their P solubility and their P speciation (Xanes, sequential P extraction), (2) their P release kinetic in soil (incubation experiment) and (3) their effect on soil P fractions and crop growth (pot and field experiments). In all experiments acidic loamy sand was used. In the main pot experiment maize, sorghum, amaranth and forage rye and in the second pot experiment maize and sunflowers were cultivated. In a two-year field experiment, the fertilizing effect of one recycled product based on Mg-P (struvite), Ca-P (Ca-SSA) and Al-P (Al-SSA) as well as the effect of N and Mg contained in struvite on crop growth and P uptake were investigated. In the first year spring barley and in the second year forage rye (catch crop) followed by sorghum (main crop) were cultivated in the field experiments.

II Main research results

In an incubation experiment the recycled products and TSP increased the concentration of labile P immediately after application, while the incubation time had a minor effect on the P solubility of the recycled products. Among the recycled products, struvite increased the labile P pools the most compared to the treated SSAs and partly even compared to TSP, which can be related to the general higher P availability of Mg-P compared to Ca-P. The effect of the treated SSAs on soil P fractions depends on the agent used for P precipitating during the P recycling process, which influenced the P speciation and the metal concentration (Mg, Ca, Al, Fe) in the SSA. In addition, the solubility of P contained in the recycled products depends on the quantity of H_2SO_4 added since raw SSAs contain generally concentrations of crystalline Ca-P, which dissolved during H_2SO_4-digestion. The thermo-chemically treated SSAs (Ca-SSAs, Mg-SSAs) were only partial-H_2SO_4-digested and consequently contain certain amounts of crystalline Ca-P (21% to 40% of Pt) (Chapter 2), while the complete H_2SO_4-digested Al-SSA contains high concentration in amorphous Al and Fe and consequently increased the P sorption capacity in the acidic soil. However, among the treated SSAs the Mg-SSAs showed higher P bioavailability than Ca-SSA since the Mg-SSAs contain lower concentrations of crystalline Ca-P compared to the Ca-SSAs. This can be related to the chlorine donor used (Ca-SSA, $CaCl_2$ vs Mg-SSA: $MgCl_2$). In addition, Mg-pyrophosphate is regarded to react in soil to plant available

P phases, while Ca-pyrophosphate and Al-pyrophosphate form less bioavailable P phases.

The higher P bioavailability of the treated SSAs and struvite compared to the SSS indicates that P recycling from wastewater treatment in form of struvite and treated SSA might not only reduce the level of contamination compared to sewage sludge, but also have a positive effect on the P bioavailability. The relative P effectiveness (related to the P uptake) of the recycled products compared to TSP increased in the order: SSS (73.0–92.2%) ≤ Al(ut)-SSA (78–89%) ≤ Al-SSA (88–98%) ≤ Ca-SSAs (90–103%) ≤ Mg-SSAs (95–121%) ≤ struvite (111–133%). The differences in the P availability can be related to the P dissolution behavior in soil and in case of the Al-SSA also to its effect on soil P sorption capacity in the acidic soil.

In addition, in the pot experiments significant interactions between crops and fertilizer treatments were found, which indicates that the efficacy of the fertilizer products also depended on the cultivated crop. The dicot crops increased the soil P fractions more compared to the monocot crops in both pot experiments, which was most likely due to the decreased soil pH after cultivation of the dicot crops.

In the field experiments also a high P fertilizing effect of struvite and the treated SSAs were found, which was comparable to TSP. The relative effectiveness of the fertilizer treatments increased in the order Ca-SSA (88%) ≤ Al-SSA (94%) ≤ struvite (106%). In addition, the Mg uptake of the crops was increased by struvite. This indicates that the crop yield was supported by the Mg fertilizing of struvite.

Struvite contains low concentrations of heavy metals. The level of heavy metals in struvite is far lower than in the SSAs and, compared to TSP, struvite contained even reduced amounts of As and Cd. The same is true for the treated SSAs in respect to the Cd concentration compared to TSP, but the SSAs contained higher concentration of other heavy metals in particular of Ni, Zn, Cu. These heavy metals can have adverse effects on crop growth and human health.

III Conclusion and Outlook

The results of this study suggest the use of treated SSAs and struvite as P fertilizers on acid soils as their effects on plant growth and soil P pools were found to be comparable to TSP. Mg-P based recycled products from wastewater, in particular struvite, can be more efficient as P fertilizer than the Ca-SSAs and the Al-SSA. Therefore, Mg based agents for P recovering from wastewater should be preferred over Ca and Al based P precipitation agents in order to increase the P bioavailability of the recycled products from wastewater treatment. Furthermore, struvite and Mg-SSAs can contribute to the Mg nutrition of crops. The low concentration of heavy metals in struvite is another reason to suggest this recycled product as fertilizer

It must be considered, that the study was carried out on sandy soils with relatively low pH values. Studies on neutral to alkaline soils may result in other values. In addition, the recycled products contain different concentrations of metals (Ca, Mg, Fe, Al; depending on precipitating agent used), which can accumulate in soil. These metals can have adverse effects on plant growth (e.g. reduction of the bioavailability of nutrient, toxic effects on crops). Therefore, the investigation of these metals in longer field experiments is necessary to exclude adverse effects on the plant-soil-system and to refine fertilizer recommendations of recycled products.

10 DECLARATION OF PRIMARY AUTHORSHIP

I declare, that I have written the present thesis for doctorate and without help of others. Other than the presented references were not used and quoted results were always marked with the relevant reference. The present thesis was never either abroad or in Germany submitted for examination in the present or a similar version.

Selbständigkeitserklärung

Ich erkläre, dass ich die eingereichte Dissertation selbständig und ohne fremde Hilfe verfasst, andere als die von mir angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe. Die vorgelegte Dissertation wurde bisher weder im Ausland noch im Inland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

Rostock, 20.03.2018

Telse Vogel