Safety and Effectiveness of Struvite from Black Water and Urine as a Phosphorus Fertilizer

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Abstract

To ensure food supply, phosphorus must be recycled, for which an appealing method is using struvite fertilizer from human excreta. One struvite from black water and another from urine were assessed for safety under Dutch regulations, and for effectiveness as P fertilizer in a maize field experiment and a literature review. Both struvites contained 12% P, 12% Mg, 6% N, and 0.5-1.5% of several micronutrients. Struvites did not exceed Dutch regulations for heavy metals or pathogens, and based on literature, organic toxins should be far below regulatory limits. In this study and 18 others, struvite appears to have similar effectiveness to soluble fertilizer. Early in the season, 200 kg P_2O_5 ha^{-1} of black water struvite and soluble phosphorus improved maize performance ($P<0.05$), however at harvest, differences in yield and biomass P content were not significant. Problems of Mg accumulation in soil can be avoided by liming and accurate fertilization. Overall, the studied struvites are safe and effective fertilizers.

Keywords: Struvite, Fertilizer, Black water, Urine, Phosphorus, Recycling, Plant availability

1. Introduction

Recently, the serious environmental problems caused by phosphorus (P) pollution have been overshadowed by the rapid depletion of global P reserves and ensuing food security concerns (Cordell *et al.*, 2009; Gilbert, 2009). Both concerns can be tackled by recovering and recycling P losses to the environment. Globally, P from human excreta accounts for roughly 12% of total losses and 33% of point source losses (Smit *et al.*, 2009). Although it is possible to produce P fertilizers from conventional sewage, it requires large amounts of energy. On the other hand, anaerobic digestion systems that mineralize organic matter by natural processes are able to produce energy and uncontaminated fertilizers from source separated human excreta (Lettinga, 2008). One product which can be produced by both conventional sewage systems and source separated urine or black water systems is struvite, normally in the form of magnesium ammonium phosphate hexahydrate: $MgNH_4PO_4 \cdot 6H_2O$.

Among various P-fertilizer products from recycled streams, struvite has advantages in simplicity of production, purity and high P-content (de-Bashan & Bashan, 2004; Winker *et al.*, 2009). Many high-tech options exist for the production of struvite, reviewed by Le Corre et al. (2009), and low tech options also exist, as demonstrated by a hand-powered reactor in Nepal (Tilley, 2009) or by mixing 3 parts stale urine with one part seawater at household scale (Author, personal experience).

Pure ammonia struvite ($MgNH_4PO_4 \cdot 6H_2O$) is by mass 44% crystal water, 39% phosphate (PO_4), 10% magnesium, and 7% ammonium. While micronutrients can be beneficial in fertilizers, other classes of contaminants, including heavy metals, pathogens, and organic toxins, are restricted under Dutch fertilizer (LNV, 2008) and EU animal byproducts regulations (ABPR 1774-2002), which are the most strict in the world (Harrison *et al.*, 1999). Before now, limited practical review of these contamination classes has been performed for struvite (Ronteltap *et al.*, 2007a; Winker et al., 2009).

Struvite is convenient in that it may be precipitated directly as fertilizer pebbles of 5 mm diameter (Giesen, 1999), or small angular crystals (Abma *et al.*, 2009) which form sticky clumps upon drying (Author, personal experience). Heating of struvite above 50 °C will lead to a simultaneous loss of water and ammonia from the struvite crystal, and at 250 °C, only $MgHPO_4$ remains (Bhuiyan *et al.*, 2008; Sarkar, 1991).

Struvite has been widely cited in wastewater treatment literature as a good P-fertilizer, and often as a slow-release fertilizer, however there is limited basis for this claim. Common phosphorus fertilizers can be divided into soluble forms such as triple super phosphate, and slightly soluble forms such as rock phosphate. Struvite does not readily fit into either category since it has low solubility (Ronteltap *et al.*, 2007b) but can decompose quickly to soluble fertilizers (Cabeza Perez et al., 2009; Johnston & Richards, 2003).

A final issue with struvite fertilizer is possible magnesium accumulation in soil. Normally, exchangeable Ca:Mg in soil ranges anywhere from 0.5:1 to 20:1, within which crop yields are not reduced (Schulte & Kelling, 2004). However, hydraulic conductivity and aggregate stability can suffer when Ca<<Mg (Zhang & Norton, 2002) as observed with Mg rich irrigation water in India (Yadav & Girdhar, 1980) and Kazakhstan (Karimov *et al.*, 2009), yet this issue has not been investigated in struvite literature.

The aim of this research was to investigate if:

(i)   struvites meet Dutch regulations for (a) metals, (b) organic toxins and (c) pathogens;

(ii)   struvites perform comparably to soluble fertilizer; and

(iii)   magnesium accumulates in soil subject to struvite fertilization.

Points (i.a), (i.c), (ii) and (iii) were investigated by experiment, and points (i.b) and (ii) by extensive literature review.

2. Materials and Methods

2.1 Struvite Production

Two struvites were used in the experiments in this study.

The first (hereafter referred to as black water struvite) was produced from effluent from a Upflow Anaerobic Sludge Blanket (UASB) reactor (35°C, HRT = 7 days) treating black water collected by vacuum toilet system from 32 houses in Sneek, The Netherlands (Zeeman et al., 2008). Struvite production involved mixing $MgCl_2$ with black water in a continuously stirred tank (100 L), overflowing into a settling tank (750 L). H_3PO_4 was added to increase ammonia removal, and NaOH was added to maintain a pH of 8.6 (Meulman *et al.*, 2007). 14 kg of roughly 0.10 mm struvite crystals was sampled after wet storage for several months and mixed thoroughly before analysis and application.

The second (hereafter referred to as urine struvite) was produced from urine feedstock acquired by GMB Slibverwerking Tiel B.V., The Netherlands, from a hormone recovery program for pregnant mothers. Again,

$MgCl_2$ addition in a completely mixed crystal growth reactor was followed by a separate precipitation tank (LeAF, 2010). The roughly 0.10 mm struvite crystals were air dried at 40 °C, and delivered in two separate batches of 10 kg each by GMB Tiel. The struvite had formed aggregates that were not completely destroyed by mixing before the experiment began.

2.2 Maize Field Experiment

The field experiment was on sandy loam soil (Typic Andosol). Phosphorus availability was low (P-Al 80 mg P kg^{-1} dry soil; Pw 8.2 mg P L^{-1}), partly caused by the low pH of the soil (4.5). Treatments included black water struvite, urine struvite, commercial triple super phosphate (TSP) and a control, in four replicates. Plot size was 4 m x 5 m. Each fertilizer was applied at 30 and 200 kg P_2O_5 ha^{-1}. Struvites were mixed with water and poured evenly onto the soil surface to avoid immediate wind erosion, and granular TSP was applied dry, by machine. Immediately after application of the phosphorus fertilizers on Day 1 (April 21, 2009), the entire field was rototilled at a depth of 15 cm, thus the average dose of fertilizer in the upper 15 cm was 110 mg P_2O_5 kg^{-1} dry soil. On Day 2, maize was machine planted. According to conventional farming practices, herbicide application and irrigation were used occasionally throughout the season. On Day 15, all plots received commercial ammonium nitrate fertilizer at 100 kg N ha^{-1}, except the 200 kg P_2O_5 ha^{-1} doses of struvite which received 80 kg ha^{-1} to partly account for the N in struvite. On Days 52, 66, 80, and 92, the performance of each maize crop stand was quantified on a scale from 0 to 10, based on visual observations. Maize crop biomass was harvested on Day 135 as 2 to 4 m of rows of all above ground biomass, and immediately shredded and dried at 105 °C. On Days 18 and 146, 3 cm cores of the top 15 cm of soil from 6 places in each plot were taken, mixed and immediately dried at 40 °C, followed by sieving at 2 mm.

2.3 Nutrient and Metal Analysis

Metal, sulfur and phosphorus levels in struvite were measured by ICP-AES after dissolution of two replicate 5 gram samples of each struvite into a clear solution of 68% HNO_3. Data reported is the average of the two replicate samples. Total N in struvite was measured by photo spectrometer (Hach Lange, Germany) after dissolution in weak H_2SO_4. Duplicate soil samples were analyzed from each plot with 200 kg P_2O_5 ha^{-1} TSP, 200 kg P_2O_5 ha^{-1} black water struvite and the control. Available phosphorus was extracted from soil by standard P-Al procedure (ammonium lactate extraction), and measured by a Segmented Flow Analyzer (SFA). Actual cation exchange capacity (CEC) was determined with an un-buffered $BaCl_2$ solution (Houba *et al.*, 1997) and the amount of exchangeable metals (Ca, Mg, Na, K, Fe, Mn, and Al) was measured in the $BaCl_2$ extract by ICP-AES. Duplicate samples of each plot of biomass were analyzed for Mg and P by ICP-AES following microwave destruction in 68% HNO_3.

2.4 Pathogen Analysis

1.5 L of raw, untreated black water and 10 L of UASB sludge were sampled directly from Decentralized Sanitation and Reuse installation in Sneek (UASB operated at 35 °C with 7 day hydraulic retention time), and refrigerated (4 °C) for less than one month until analysis, at which time samples were shaken and mixed thoroughly. Pathogen analysis of struvite, black water and UASB sludge was done by dilution of 10 g of sample in 100 mL demi water in a sterile stomacher bag, and mixed for 2 minutes. Detection and enumeration of Enterobacteriaceae was done by plating each sample on six replicate plates at 37 °C on Violet Red Bile Glucose Agar (VRBGA), based on ISO 21528, in accordance with EU Animal By-products Regulations, ABPR 1774-2002. Colonies were confirmed and identified to the species level by oxidase test, aminopeptidase test, microscopy, oxidation fermentation agar (OFA) test, and BBL Entereotubes.

2.5 Statistical Analysis

Averages of data across the four replicate plots of the maize experiment were compared based on their means by one way Anova test with post-hoc Tukey test by PASW SPSS software.

2.6 Literature Review

On two topics, data from literature has been compiled and analyzed.

The first topic is the levels of metals and persistent organic toxins in human excreta, which are relevant under fertilizer regulations. Data is expressed as milligrams of metal or organic compound per kg of P_2O_5, based on an average total per capita excreta stream of 2 g P day^{-1} (Heinonen-Tanski & van Wijk-Sijbesma, 2005; Kirchmann & Pettersson, 1995).

The second topic is plant availability studies with struvite. 19 different studies (Table 4) were found which investigated fertilizer effectiveness and/ or plant availability of P from struvite.

3. Results

3.1 Nutrient Composition and Contamination of Black water and Urine Struvite

Both struvites had similar composition of roughly 12% P and Mg, and 0.25 to 5% N, Ca, Fe, S, Na, and K as weight fractions of total solids (Table 1).

From literature, zinc levels in untreated human feces exceed Dutch fertilizer regulations, however metal levels in struvites were less than 15% of the maximum level in regulations (Table 2).

Raw black water contained 36200 colony forming units (CFU) per gram of enterobacteriaceae, including pathogens *Klebsiella pneumoniae, Proteus mirabilis,* and *Enterobacter agglomerans*, whereas zero enterobacteriaceae were found in either struvite. EU regulation ABPR 1774-2002 allows a maximum level of 1000 CFU g^{-1} in recycled organic waste products. The sludge in the UASB reactor contained 100 CFU g^{-1}, including *E. Coli.*

The compounds closest to legal thresholds for organic toxins were pesticides aldrin, deldrin, and DDT, as well as PAH's naphthalene and hydroxyfluorene, which were roughly 1 to 5% of fertilizer regulations (Table 3).

3.2 P Availability to Plants and the Behavior of Struvite in the Soil

Until halfway through the growth period (Day 66) the maize treated with black water struvite, and triple super phosphate (TSP) at 200 kg P_2O_5 ha^{-1} was rated significantly ($P<0.05$) better than the control, as indicated by stars in Fig. 1. Urine struvite did not produce significant improvements in maize growth, however early in the season, a dose-performance trend was apparent for all P fertilizers in Fig. 1. At harvest, there was no significant differences between dry matter yield (averaging 23 tonnes per hectare) and P uptake (averaging 70 kg P_2O_5 ha^{-1}) across all treatments, which indicates P was not limiting maize growth in this experiment.

Fig. 2 shows phosphorus availability in the soil in TSP, black water struvite and control plots, at Days 18 and 146. Both at the beginning and the end of the season, soil amended with TSP and blackwater struvite had higher available P.

Many pot studies showed struvite treatments to perform similarly to soluble P fertilizer treatments, and not insoluble fertilizer treatments (Table 4), while one study found struvites performance was between soluble and insoluble fertilizers (Massey *et al.*, 2009). The literature studied had three field scale experiments. These showed increases in available P after struvite application (Bridger *et al.*, 1962; Cabeza Perez et al., 2009; DLV, 2008), but did not show differences as clearly as pot experiments. None of the studies in Table 4 indicated that struvite exceeded any regulatory limits or reduced crop growth significantly. Eight studies specifically investigated safety issues of struvite as fertilizer, and again found no intrinsic problems. Metal contamination was investigated and posed a risk from dirty feedstock in some cases (Abma et al., 2009; Escher *et al.*, 2006; Goto, 1998; Li & Zhao, 2003; Matsumiya *et al.*, 2000; Schuiling & Andrade, 1999; Ueno & Fujii, 2001; Weinfurtner *et al.*, 2009). One study investigated plant growth in pure struvite (Bridger et al., 1962) and another with very high doses (Li & Zhao, 2003), and still found no problems with plant growth!

Fig. 3 shows levels of magnesium in maize and soil in plots amended with black water struvite and TSP at 200 kg P_2O_5 ha^{-1} and the control. Blackwater struvite at 200 kg P_2O_5 ha^{-1}, increased Mg levels by 28% in biomass ($P<0.05$) and 100% in the soil ($P<0.05$) compared to the control and TSP plots. No significant differences were found in terms of total cation exchange capacity of the soil and levels of Al, Ca, K, Na, Fe and Mn (Tukey test, $P >0.10$; data not shown).

4. Discussion

4.1 Nutrients and Metals in Black water and Urine Struvite

The wide range of essential plant nutrients (K, Ca, S, Na and Fe) present at levels of near 1% may be a positive quality for struvite as a fertilizer, and extend the function of struvite to recycling more than just the N and P.

Heavy metals do not appear to be a regulatory problem for the use of source separated human excreta struvite products as fertilizer. Heavy metals are higher in urine struvite than in blackwater struvite, probably because (1) metals are removed from blackwater in the UASB reactor preceding struvite precipitation (de Graaff, 2010), and also because, H_3PO_4 was added to precipitate more NH_4 from the wastewater, and thus, metal contaminants were diluted into more struvite. Heavy metals may contaminate struvite by replacing Mg, NH_4 or PO_4 in the crystal structure (Ronteltap et al., 2007a), or as co-precipitates, for example as sulfide salts. Because the rates of recovery of P from black water and urine are greater than 90% (LeAF, 2010; Meulman et al., 2007), levels of heavy metals can not be concentrated to more than 111% of their original content in human excreta, per P, and therefore such struvites can be considered safe products with regard to heavy metals.

4.2 Pathogens in Black water and Urine Struvite

No published literature has been found which quantifies pathogen levels in struvite, despite recent reviews highlighting the critical importance of pathogen reduction in fertilizer products from sanitation (Arthurson, 2008; Winker et al., 2009).

Pathogen levels in urine are generally very low, and therefore the lack of pathogens in urine struvite is not surprising and does not demonstrate a reduction of pathogens during struvite precipitation.

On the other hand, high levels of enterobacteriaceae levels in raw black water (36200 CFU g^{-1}), do pose a risk. The 2 log10 reduction (>99 %) to 100 CFU g^{-1} in UASB sludge is reasonable when compared to efficient, well mixed mesophillic digesters (Smith *et al.*, 2005). The storage of UASB sludge for several weeks in a refrigerator may also have lead to the reduction of pathogens, and thus further analysis of pathogen reduction in these UASB reactors is recommended. Still, the undetectable levels of pathogens in the struvite indicate that further reduction of pathogens may occur during struvite precipitation.

A mechanism by which pathogens may be reduced during struvite production is exposure to high salinity during dewatering, drying and storage. Enterobacteriaceae are resistant to oxygen and ammonia but are inhibited by high salinity (Müller *et al.*, 2006). Fecal coliform survival time decreased by 55% with each 5% increase in salinity, from a salinity of 0 to 5 Sm^{-1} (Solic & Krstulovic, 1992).

4.3 Organic Toxins in Black water and Urine Struvite

Literature values for organic toxins in human excreta indicate that levels of organic toxins in struvite will remain below Dutch fertilizer regulations. This statement relies on the assumption that substances other than human excreta, such as toxic cleaning products are not deposited in the toilet.

Other classes of organic toxins that may be of concern in fertilizers, not yet listed under regulations, include phenols, hormones, pharmaceuticals, plasticizers and other chemicals for crop protection (de Mes, 2007; Fatiadi, 1984). In the field of human health, a wide variety of herbicide, pesticide and plasticizer residues have been quantified in human intake and/or excreta (Fromme et al., 2009; Hill et al., 1995; Nasreddine & Parent-Massin, 2002; Ye et al., 2008), however the field of wastewater treatment has focused on estrogenic pharmaceuticals and hormones (de Graaff, 2010; Maurer *et al.*, 2006; Winker et al., 2009). Escher (2006) found that less than 1 to 4 % of the spiked hormones and pharmaceuticals in the urine feedstock were present in the struvite product, which is a better performance than a bioreactor, nanofiltration, ozonation or UV. A related study found that seven non-ionic, acidic and basic hormones and pharmaceuticals stayed in solution >98% during struvite crystallization from urine (Ronteltap et al., 2007a). Thus, organic toxins tend not to precipitate with struvite, making struvite an attractive option for avoiding organic toxins.

In contrast to the persistent organic pollutants in Table 3, estrogenic hormones are degradable in aerobic soil with a half life of days (Scherr *et al.*, 2008; Xuan *et al.*, 2008). However, as the investigation of hormone mimicking compounds in wastewater is still a new area of research, there are entire classes of similar compounds which are virtually uninvestigated (Streck, 2009).

4.4 Plant Availability of Nutrients from Struvites

Overall, black water struvite performed similarly to triple super phosphate (TSP), increasing overall crop stand performance (P<0.05). These results support previous research showing that struvite performs comparably to a soluble P source such as TSP (Table 4).

The release of nutrients from urine struvite appeared to be slower than TSP and blackwater struvite, since it did not improve growth rates significantly, early in the season. This could be because struvite particles from urine were clumped together and thus had lower surface area than blackwater struvite, which may account for the slower release of nutrients. If further research indicates that this is in fact the mechanism controlling the release of mineral nutrients from the two struvites, different sizes of granules can be made easily during drying of struvite, as it has happened naturally in this case, to control the temporal pattern of nutrient release.

Struvites gave similar yields to TSP, but neither fertilizer significantly increased yield compared to the control, meaning that another factor was limiting maize growth at the end of the season (not available P in the soil). Therefore, no clear statements on the fertilizer value of struvite can be made, except that no negative effects were observed with struvite application.

There exists a convincing body of literature produced during the past half-century that indicates that N, P, and Mg from struvite have good plant availability across a wide range of soils and crops (Table 4). Several studies also note positive effects of magnesium availability for crops. Furthermore, no study has shown negative effects from struvite application, even with seed germination in pure struvite (Bridger et al., 1962) and struvite

application at extremely high doses (Li & Zhao, 2003). Thus, for plant growth, we expect further research to show that struvite can be considered a safe and effective fertilizer.

4.5 Solubility and the Behavior of Struvite in Soil

The high dose of 200 kg P_2O_5 ha^{-1} of black water struvite and TSP increased P-Al at similar magnitude, compared to the control, at both the beginning and the end of the season, comparable to a similar study by Cabeza-Perez et al. (2009) which found that TSP always yielded higher P-Al and rock phosphate always yielded lower P-Al than struvites, at harvest.

To explain and predict nutrient release from struvite in the soil, solubility of struvite must be understood. The solubility of struvite changes with pH, temperature and ionic strength (Le Corre et al., 2009).

Struvite reached a minimum solubility of 0.040 mM at pH 8.2 to 8.8 (Le Corre et al., 2009) whereas at pH < 5, struvite dissolved above 1 mM (Abbona *et al.*, 1982), and even above 10 mM (Borgerding, 1972). The range of normal pH in soil is from 4.5 to 8.5, thus more acid soils will lead to quicker dissolution of struvite.

The solubility of struvite also changed dramatically with temperature, peaking at 2 mM at about 20 °C, compared to 1mM at 0 and 50 °C in the same solution (Borgerding, 1972).

From reported pK_{SP}'s (log of molar solubility product) in pure water (pK_{SP} = 12.60), struvite can dissolve to 0.063 mM (Michalowski & Pietrzyk, 2006), whereas in urine, with ionic strength of 0.40 M (pK_{SP} = 13.26) struvite will dissolve to 0.038 mM (Ronteltap et al., 2007b). The ionic strength of soil moisture is generally around 0.10 M and thus the solubility in soil will be between these values, still depending on temperature.

Regardless of the exact solubility product, the concentrations of Mg^{2+}, NH_4^+ and HPO_4^- ions in soil solution ultimately determine the dissolution of struvite, and are mainly dependent on soil type and moisture content (Dyer *et al.*, 2008). In soil moisture, typical concentrations are 0.1 to 15 mM Magnesium (Adams, 1971; Dyer et al., 2008), 0.01 to 1 mM orthophosphate (Adams, 1971; Edmeades *et al.*, 1985), and 0.01 to 100 mM ammonium and ammonia (Edmeades et al., 1985; Smethurst *et al.*, 2001). Thus struvite may dissolve in a typical soil, especially in soils with low ammonia levels.

Bridger et al., (1962) argues that the nitrification of ammonium often limits the dissolution of struvite. In aerobic soil, the concentration of nitrate is much higher than ammonium in solution, due to rapid conversion process from ammonia to nitrate by bacteria. This biological process is dependent on temperature, other nutrients, oxygen and microbial community composition. Further experiments with nitrification inhibitors, sterile soil, and varying temperatures support the theory that nitrification of ammonia often limits struvite dissolution (Rothbaum & Rohde, 1976). In a fertile aerobic soil, ammonium can be converted to nitrate within days, whereas some anaerobic soils have permanently high ammonium levels in which case another process might be limiting dissolution. Thus, this mechanism can explain plant availability, as reported in Table 4.

4.6 Magnesium Accumulation

The 28% increase in magnesium content in the maize biomass due to struvite is not expected to have an important effect on the nutritional value of maize for humans or animals (Toba et al., 1999).

Application of magnesium (Mg) in black water struvite at 200 kg P_2O_5 ha^{-1} caused a two fold change in exchangeable Ca:Mg ratio of the soil from roughly 4:1 to 2:1 over 146 days (P<0.05), indicating that over several years of this rate of struvite application, the soil physical properties such as hydraulic conductivity and aggregate stability may begin to deteriorate (Zhang & Norton, 2002).

The total cation exchange capacity (CEC) of the field plot soil of 3 cmol kg^{-1} was very low, indicating that this field had poor buffer capacity for water, pH and nutrients compared to most soils with CEC of 10 to 50 cmol kg^{-1} (Parfitt *et al.*, 1995). Furthermore, in this experiment, the rate of P application (200 kg P_2O_5 ha^{-1}) was excessive compared to the crop uptake (70 kg P_2O_5 ha^{-1}). For context, a soil with CEC of 35 cmol kg^{-1} and struvite application rate of 50 kg P_2O_5 ha^{-1} would take at least 50 years to reach a 2 fold change in Ca:Mg ratio.

Plants uptake P and Mg in similar proportions to those applied by struvite. In a soil with CEC = 10 cmol kg^{-1}, 50% Ca and 15% Mg, molar ratios of Mg:P for maize uptake was found to be roughly 1.3:1 to 2:1 (Estes, 1972), whereas struvite contains Mg:P at a molar ratio of 1:1. Therefore, if struvite fertilization is not excessive on a P basis, it will not be excessive on a Mg basis.

Still the Ca:Mg ratio will change if Mg is added and Ca is not. Estes (1972) also found that maize uptake of Ca and Mg was roughly equal on a molar basis. Thus quantities of calcium must be replenished, perhaps by liming, at the same molar rate that struvite is applied to maintain a healthy Ca:Mg ratio over the long term.

5. Conclusions

Struvites from urine and anaerobically digested black water were assessed for safety and effectiveness as phosphorus fertilizers. It was found that:

• Both struvites contained levels of P (12 %), N (5 %) and Mg (11-14 %) suitable for use as macronutrient fertilizer; for comparison, the P content of triple super phosphate is 19 %.

• Both struvites contained quantities of Fe, Na, Ca, S, and K which may supplement their value as fertilizers.

• Both struvites were within Dutch regulatory limits for heavy metals and pathogens, and in general, struvites produced from the same feedstock are also likely to pass these regulations.

• From literature, organic contamination in human excreta feedstock is 95% lower than in Dutch fertilizer regulations and less than 4% of organic contamination in the feedstock is expected to precipitate with struvite.

• Based on 24 studies, plant availability of P from struvite is often comparable to that of soluble fertilizer.

• No problems are expected from magnesium addition to soil by struvite, when P over-fertilization is avoided and calcium extracted by crops is replenished.

• Overall, the struvites studied are safe and effective P fertilizers. Based on the findings presented in this paper, the Dutch Ministry of Agriculture has indicated that it is likely to approve an application to trade similar struvite fertilizer products in the Netherlands.

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Table 1. Main components of urine and black water struvites, as a weight fraction of total solids (TS)

	Blackwater Struvite (% of TS)	Urine Struvite (% of TS)
P	11.91	11.66
Mg	10.68	13.97
N	5.38	5.26
Ca	1.37	0.96
Fe	0.74	0.48
K	0.41	0.24
Na	0.87	0.51
S	0.98	0.74

Table 2. Levels of heavy metals in raw human excreta, black water and urine struvite, other struvites from literature, and Dutch fertilizer regulations (in mg kg^{-1} P_2O_5)

	Human Urine	Human Feces	Struvite Urine	Struvite Blackwater	Struvite Potatoes	Struvite Sewage	Fertilizer Regulation
Cd	3	15	< 6	< 4	0.9	0.2	31.3
Cr	13	29	< 6	< 4	17	< 677	1875
Cu	169	1595	336	134	42		1875
Ni	126	108	6	< 2	26	< 31140	750
Pb	20	29	< 81	< 59	6.6	< 0.17	2500
Zn	291	15551	841	< 59	336	< 338	7500
Hg	1	13			< 0.3		18.8
As			< 42	< 24	< 6	2	375
Refs.	[1]	[2]	[3]	[3]	[4]	[5]	[6]

Refs: [1] - (Ronteltap et al., 2007a), [2] - (Kujawa-Roeleveld & Zeeman, 2006), [3] - this study, [4] - (Abma et al., 2009), [5] - (Ueno & Fujii, 2001), [6] - (LNV, 2008)

Table 3. Levels of organic contaminants in raw human excreta which are specifically restricted by Dutch fertilizer legislation. Organic contaminants in raw human excreta as restricted by Dutch fertilizer legislation, EU and global restrictions and observed values from literature

Organic Compound	Contamination Rate (in mg kg^{-1} P_2O_5)				Restrictions	
	Regulation	Excreta	Urine	Urine		
	Netherlands	Sweden	Canada	Italy	EU	Global
HCB, hexachlorobenzene	31	0.025	0.102		EU	SC
Σ HCHs	310	0.018				
γ-HCH (Lindane)	1.2				EU	SC
Σ aldrin/ deldrin	7		0.152			SC
Σ endrin/isodrin	7		0.076			SC
Σ DDT/DDD/DDE	23	0.114	0.991		EU	SC
Σ PCDD/PCDF (Dioxin)	0.019	1.19E-05			EU	SC
Σ 6 PCB (excl PCB 118)	375	0.134	0.381		EU	SC
Σ 10 PAK (PAHs)	11500				EU	SC
PAH naphthalene	600			13.43	EU	SC
PAH hydroxyfluorene	270			2.42	EU	SC
PAH hydroxyphenanthrene	750			0.73	EU	SC
Minerale oil	935000					
Refs.	[1]	[2]	[3]	[4]	[5]	[6]

Refs: [1] - (LNV, 2008), [2] - (Darnerud et al., 2006), [3] - (McLeod *et al.*, 1980), [4] – high exposure asphalt workers (Van Rooij *et al.*, 1994), [5] – (Erhardt & Prüeß, 2001), [6] – Stockholm Convention on POPs (UNEP, 2001)

Table 4. List of experiments reporting the fertilizer value of struvite

Citation	Year	Type	Crop	Struvite Source	Improvement in crop*		
(Bridger et al.)	1962	pot	Herbaceous flowers, tomatoes	USA, chemical reagents	0-100	NR	SOL
(Bridger et al.)	1962	field	Shrubs, grasses	USA, chemical reagents	40-75	NR	
(Terman & Taylor)	1965	pot	Maize	USA, chemical reagents	40	SS	
(Ghosh *et al.*)	1996	pot	Chickpea, gram	India, chemical reagents	50	SS	SOL
(Goto)	1998	pot	Komatsuna, green vegetable	Japan, "recovered" struvite	50	SS	SOL
(Johnston & Richards)	2003	pot	Ryegrass	UK, chemical reagents	100	SS	SOL
(Johnston & Richards)	2003	pot	Ryegrass	Japanese sewage, and Dutch sewage & manure	100	SS	SOL
(Johnston & Richards)	2003	pot	Ryegrass	Spanish red dye liquor, US corn liquor	100	SS	SOL
(Li & Zhao)	2003	pot	Cabbage, chard, spinach, etc	Hong Kong, landfill leachate	>100	SS	
(Romer)	2006	pot	Ryegrass	German and USA manure	>100	SS	SOL
(Romer)	2006	pot	Ryegrass	German, Italian, and Japanese sewage	>100	SS	SOL
(Gonzalez Ponce & Lopez-de-Sa)	2007	pot	Perennial ryegrass	Spain, municipal wastewater		SS	>SOL
(Montag *et al.*)	2007	pot	unspecified	Germany, sewage sludge		NR	SOL
(Plaza et al.)	2007	pot	Ryegrass	Spain, municipal wastewater	>100	SS	SOL
(Ganrot *et al.*)	2007	pot	Wheat	Sweden, human urine, also included zeolites	30-100	SS	
(Ponce & Lopez-de-Sa)	2008	pot	White lupine	Spain, municipal wastewater		NR	SOL
(Cabeza Perez et al.)	2009	pot	Maize	Germany, sewage sludge	25-100	SS	SOL
(Cabeza Perez et al.)	2009	field	Rapeseed and winter barley	Germany, sewage sludge	0-40	NS	SOL
(DLV)	2009	field	Flowers, potatoes, Brussels sprouts	Netherlands, potato wastewater		NR	
(Massey et al.)	2009	pot	Spring wheat	USA, dairy waste and process wastewater	<25	SS	<SOL
(Gonzalez Ponce *et al.*)	2009	pot	Lettuce	Spain, municipal wastewater		SS	SOL
(Weinfurtner et al.)	2009	pot	Maize	Germany, sewage sludge	20-100	SS	SOL
(Yetilmezsoy & Sapci-Zengin)	2009	pot	Purslane, cress, grass	Turkey, digested poultry manure	>100	NR	
(This study)	2010	field	Maize	Netherlands, urine and black water	<30	NS	SOL

* Number refers to % improvement over control in P-uptake and/or yield; SS = improvement is statistically significant; NS = improvement is not statistically significant; NR = statistics not reported; SOL = comparable to soluble fertilizer.
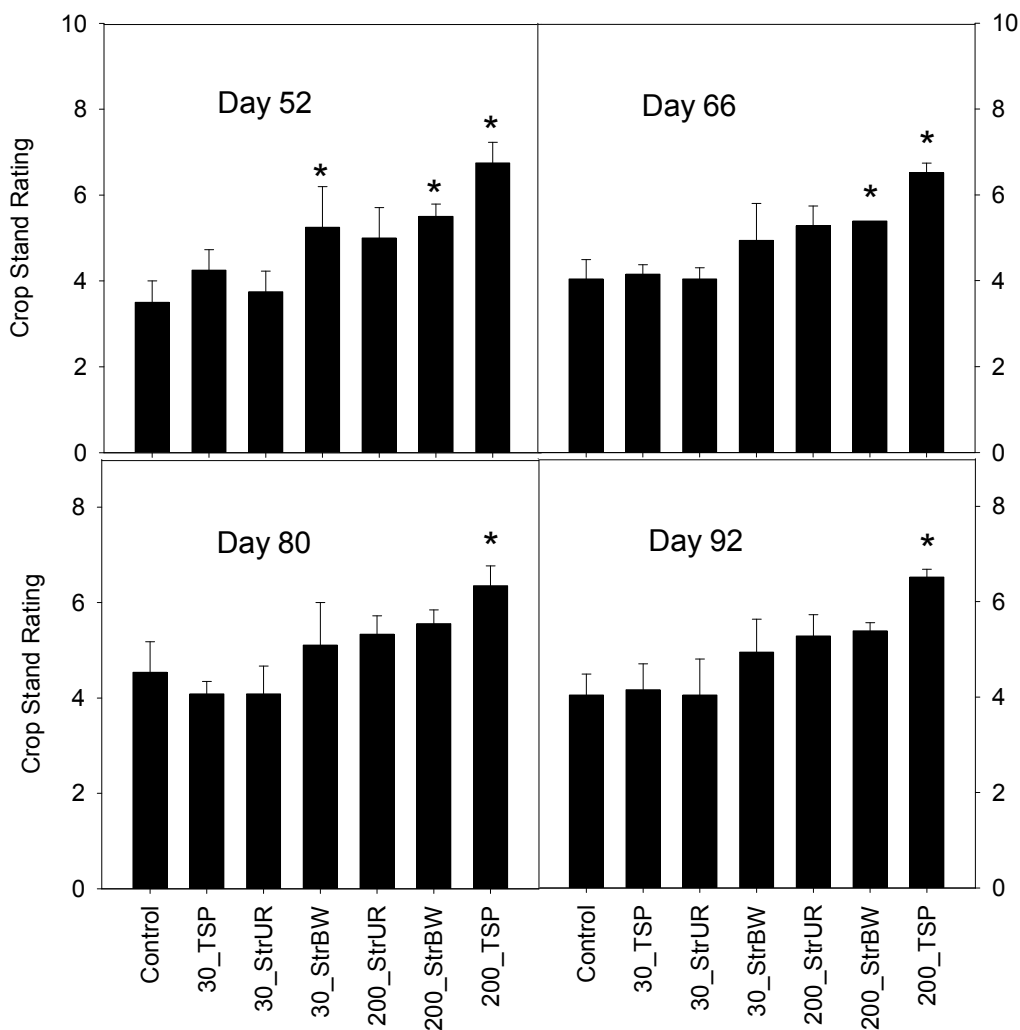
Figure 1. General crop stand evaluation from visual inspection, over the growth period for struvite and TSP plots.
Error bars indicate standard error, n = 4; * stars indicate significant difference over the control, Tukey (P < 0.05);
TSP refers to triple super phosphate, StruBW and StruUR refer to blackwater and urine struvite respectively; 30
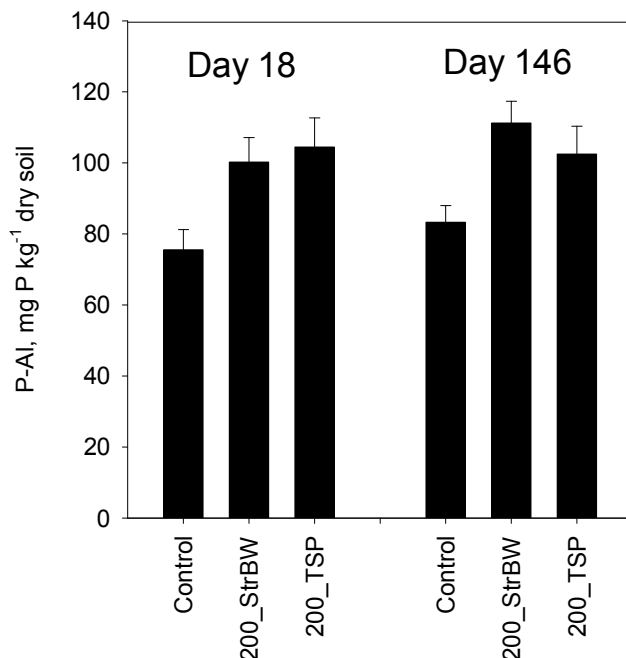and 200 refer to fertilizer dose in kg P_2O_5 per ha

Figure 2. Soil available phosphorus (P-Al) at Days 18 and 146 for control, black water struvite, and triple super phosphate (TSP) treatments. Error bars indicate standard error, n = 4, there were no significant differences (Tukey, P<0.05) ; TSP refers to triple super phosphate, StruBW and StruUR refer to blackwater and urine struvite respectively; 200 refers to fertilizer dose in kg P_2O_5 per ha
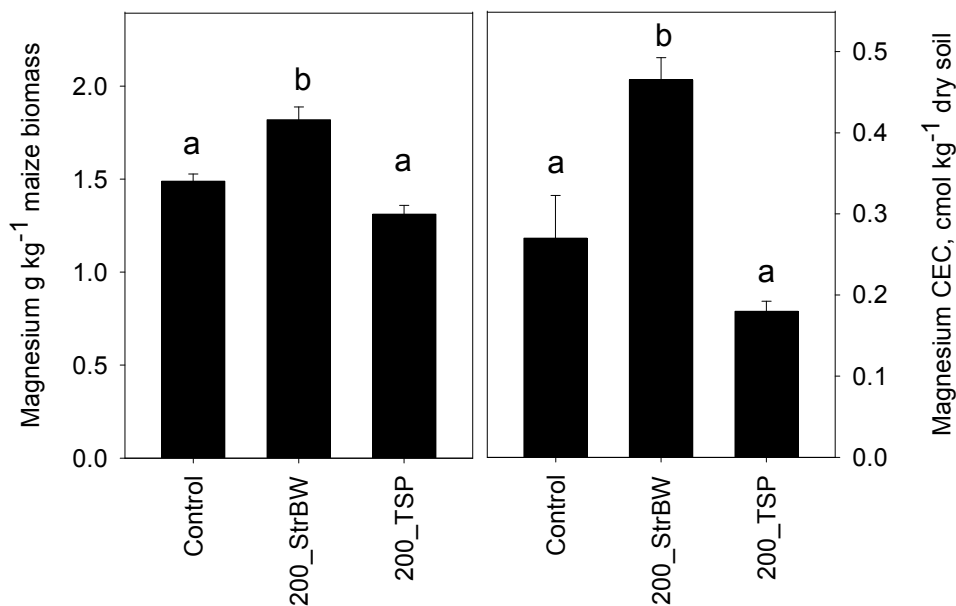

Figure 3. Magnesium levels in maize biomass (left) and soil (right) at the end of the season, Day 146. Error bars indicate standard error, n = 4; letters indicate significant differences, (Tukey P < 0.05); TSP refers to triple super phosphate, StruBW and StruUR refer to blackwater and urine struvite respectively; 200 refers to fertilizer dose in kg P_2O_5 per ha