Assessment of Alternative Phosphorus Fertilizers for Organic Farming: Sewage Precipitation Products

The application of sewage sludge to agricultural land is currently prohibited in organic farming due to the risk of soil contamination from harmful compounds. Incineration or disposal to landfill of sludge is costly, leads to increased greenhouse gas emissions, and neglects the possibility of nutrient recovery. There are various technologies to recover P by crystallization or precipitation from waste water and sewage sludge. Depending on the input material, nutrient concentrations and concentration of contaminants can vary widely. Regarding the content of potentially toxic elements, the trade-offs between (potentially) toxic element concentrations and potential benefits may be more favorable for treated sewage products than for several natural phosphate rocks or even animal manures or bio-waste compost. This fact sheet describes the most important aspects to assess the suitability of sewage sludge precipitation products for use in organic farming.

Introduction
Phosphorus (P) in sewage sludge accounts for a significant portion of the potential P resources for recycling in European societies, e.g. more than 50% of the non-agricultural sources in Germany[1]. Consequently, several pioneers of organic farming at the beginning of the 20th century based their fertilization strategy on recycling of urban organic wastes including human feces[2].

Currently the use of sewage sludge is forbidden in organic farming[3] because of the risk of contamination by toxic elements and other harmful substances including human pathogens and drug residues[4]. The decision not to use sewage sludge as a fertilizer has unintended consequences in terms of increased greenhouse gas (GHG) emissions from sludge incineration, higher disposal costs, loss of nutrients like nitrogen (N), P and potassium (K), and loss of organic matter[5, 6].

Separation of P and other plant nutrients like N, magnesium (Mg) and K by precipitation or crystallization may be an option to recover purified P and recycle it, with reduced risks for contamination compared with applying sewage sludge directly to the soil.
Production of precipitation products from sewage sludge

The yearly available sewage sludge production in the European Union is 11 million tonnes dry mass (DM)\(^7\). Precipitation treatment procedures can recover ortho-P and chemically dissolvable phosphates of Ca, Fe, Al, etc. from different sources including sewage sludge, urine and other wastewater.

Standard methods for recovering P from process waters and stabilized sludge

There are multiple available technologies to recover P. The primary treatment of any sewage usually consists of temporarily holding the sewage in a basin for «preliminary clarification» where heavy solids can settle down to the bottom while lighter components float to the surface (Figure 1). The settled and floating materials are removed and called "primary sludge". The remaining liquid (process water) contains dissolved substances including plant nutrients like ortho-P, ammonium and K, as well as dissolved and suspended biological matter. Therefore, further treatment is necessary to separate N and P from this liquid phase and to prevent these nutrients from contributing to eutrophication of water bodies.

The secondary treatment of the waste water stream, called "aeration", is typically performed by indigenous, water-borne micro-organisms in a managed process to remove N by denitrification, and to remove P either by enhanced biological P removal (using the ability of some micro-organisms to accumulate phosphates as polyphosphates for their own metabolism) or by application of chemicals like iron (Fe\(_{3}\)P, Fe\(_2\)(SO\(_4\))\(_3\)), alum (Al(SO\(_4\))\(_3\)) or lime (Ca(OH)\(_2\)) which form insoluble precipitates with P. The secondary treatment also requires a clarification step to remove the micro-organisms and/or precipitates from the treated water prior to discharge. The solid phase (called "activated sludge") produced by this secondary clarification treatment can be added to the "primary sludge" obtained in the first step\(^8\). The sludges from the different processes are then biologically stabilized (e.g. by anaerobic digestion) where the easily available organic matter is degraded.

The stabilized sludge or digestate can be directly used as fertilizer (usually de-watered or dried after a solid-liquid separation), enabling the recycling of the remaining N, S and K, as well as almost all P (organic and inorganic P forms). Substances like organic pollutants and toxic elements are not (or only partially) removed by the stabilization process. Hence, further treatment of stabilized sludge may improve its quality as a fertilizer for use in agriculture.

Precipitation and crystallization products could be obtained from the process waters obtained during the different treatment steps of sewage (e.g. after the solid-liquid separation of the influent sewage at the beginning of the treatment process, or after anaerobic digestion of the sludge at the end of the overall sewage treatment process). There are two possible ways of P precipitation from stabilized sludge, which can be performed either before de-watering, enabling higher P recovery rates, as the whole sludge stream is treated, or after the de-watering of the sludge, enabling lower P recovery rates by a chemical treatment, as only the liquid phase is treated.

Figure 1: Standard method for sewage treatment and P recovery in wastewater treatment plants
Improved methods for recovering P from process waters and stabilized sludge

In this fact sheet, basically three processes for recovery of P are described, leading to two different P fertilizer types, calcium phosphates and struvite.

Precipitation of Calcium-Phosphate from process waters

Ortho-P anions precipitate in the presence of Ca as calcium phosphates (Ca-P). The higher the pH, the stronger the building of precipitates. One method is the phosphorus recovery from waste and process water by crystallization (P-RoC® process) which was developed at Karlsruhe Institute of Technology (KIT) [11] (Figure 2).

Another approach for production of Ca-P from process waters is the Budenheim Carbonic Acid process (Figure 3). In this process the pH influencing effects of dissolved bi-carbonates (HCO$_3^-$) are selectively used by addition or removal of CO$_2$ according to the formula:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \rightarrow 2\text{H}^+ + \text{CO}_3^{2-}$$

Each addition of CO$_2$ shifts the reaction equilibria to the right, leading to a release of protons (H$^+$) and a decrease of the pH, while removal of CO$_2$ increases pH. When CO$_2$ is added under high pressure the acidic conditions created dissolve the inorganic phosphates.

The recovery rate from this process to date is 50%, and about to be increased up to 70% compared to the total P in the influent of waste water treatment plants (WWTPs). A major advantage of this process is the absence of chemical inputs other than Mg-salts and CO$_2$, which is recycled. Comparative data on energy requirements are not available.

In the P-RoC-process Calcium silicate hydrate (CSH) pellets or granules are added to the process water releasing hydroxide ions. The resulting increase in pH leads to the crystallization of struvite, hydroxyapatite or brushite. The end product can be mono-calcium phosphate (MCP), di-calcium phosphate (DCP) and/or tri-calcium phosphate (TCP).

In this process inorganic phosphates in the primary sludge are dissolved under acidic conditions created by addition of CO$_2$ under high pressure. This process step is followed by a solid-liquid separation. The CO$_2$ is then removed from the P-enriched liquid phase by a reduction in pressure and application of a vacuum, leading to a strong increase in pH, and subsequent P precipitation or crystallization. CO$_2$ is recycled and can be used again.
**Struvite crystallization**

Another approach aims at enhancing crystallization of Magnesium ammonium phosphates (struvite) from both solid phases and process waters during the treatment process. P crystallization to struvite can be performed at different process steps and in different ways:

a) Direct P precipitation to struvite from the non-dewatered sludge with relatively low P recovery rates. Examples: AIRPREX, NUReSyst, Fixphos.

b) Chemical re-dissolution of phosphates of Ca, Mg, Al and Fe as well as other metal phosphates e.g. by addition of H₂SO₄, HCl, CO₂ or H₂O₂ leading to the transformation of (Ca, Mg, Fe, Al, other metal) phosphates to ortho-P. This is followed by a mechanical separation step, and sometimes the addition of chelates like citrate to keep potentially toxic elements in solution. The final step involves P precipitation as described in figure 3. Examples: Gifhorn, Stuttgart, Verfahren.

c) Solid-liquid separation of the stabilized sludge with disposal or incineration of the solid phase (leading to a P rich ash), with removal of the dissolved ortho-P in the process water by crystallization. Examples: Pearl, NuReSys, Airprex. For example, in the Stuttgart process (developed at the Institut für Siedlungswasserbau, Wassergüte und Abfallwirtschaft ISWA, Stuttgart, Germany) (Figure 4).

In all treatment procedures based on chemical dissolution of P, like the Stuttgart process, the acid requirements and therefore the separation cost are influenced by the Fe content of the substrate, and therefore also by the P precipitation method during the secondary clarification of the process wastewater (biological or chemical precipitation) before release to the water bodies. Other factors influencing the acid requirement are the NH₄⁺-content as well as the amounts of dissolved CO₂ as the two main buffering substances in manures and sludges.

An important disadvantage of precipitation procedures are the limited recovery rates of P in the precipitated product (from 5% for direct precipitation to 65% for dissolution and precipitation) of the total sewage plant P influx[8]. The higher the recovery rate, the higher the specific acid consumption for re-dissolution and the higher the cost of the treatment procedure.

Important advantages for the operator of the treatment plant are less incrustation of struvite in pipes and a reduced nutrient return load of the process water as well as easier dewatering of the sludge (when the recovery is applied prior to dewatering), resulting in considerable cost savings in the sludge dewatering procedure. The value of these cost savings is higher than the monetary value of the P fertilizer product[8].

**Fertilizer nutrient concentration and characteristics**

**P content and P speciation**

The complete name of struvite is magnesium ammonium phosphate hexahydrate, and it consists of Mg²⁺, NH₄⁺, and PO₄³⁻ ions in the molar ratio of 1:1:1 (MgNH₄PO₄ • 6H₂O). Other crystals belonging to the struvite group are MgKPO₄ • 6H₂O, CoNH₄PO₄ • 6H₂O, CoKPO₄ • 6H₂O, NiNH₄PO₄ • 6H₂O and NiKPO₄ • 6H₂O[14]. Depending on the P-load of the raw material and the production process, total P concentrations of the struvite range between 11–26% (Table 1) of which 1–2% is water soluble and about 50% is soluble in citric acid (2%) [14, 15, 16].

The precipitation product of the P-RoC© procedure is calcium phosphate, which contains up to 13% P (Table 1). Ca-P precipitates will be a mixture of di-hydrogen phosphates (H₂PO₄⁻, primary phosphates), hydrogen phosphates (HPO₄²⁻ secondary phosphates) and ortho-P (PO₄³⁻ tertiary phosphates). The solubility of the precipitate will increase with an increasing proportion of tertiary phosphate.

**Plant P bioavailability of struvite and Ca-P**

Pot experiments on P-availability have been conducted on maize plants with a wide range of struvite and Ca-P products derived from sewage sludge and process water[15, 26, 27, 28]. Struvite products showed a high bioavailability in both acid and calcareous soils, which was comparable to the availability of triple superphosphate (TSP).
more plant available than Ca phosphates at alkaline 
pH, and hence it is a potential P fertilizer in calcar -
eous soils [29]. This shows that the water solubility 
of P fertilizers and their plant availability in the soil 
are not necessarily related. Ca-P products are gener-
ally less soluble, with a solubility in water ranging 
from 0 to 50 %. MCP and DCP have a high short 
term fertilizer efficiency (e.g. from P-RoC © or Bud- 
denheim process), while plant P availability of TCP 
is low [27, 28]. The plant availability is dependent on 
soil pH, with higher solubility in acid soils due to 
a higher H+-concentration [15]. The solubility of Ca-P 
products is further dependent on the granulate size 
[29].

Other nutrients, their speciation 
and plant bioavailability

The two other main nutrients contained in struvite 
are Mg (5–10 %) and N (1–5 %) as NH4+. Struvite can thus be used as a compound 
fertilizer. Further mineral elements may be con-
tained in small amounts like Ca, K, Na, Al, and Fe 
depending on the production process (Table 1). 
Ca-P products adsorbed to CSH particles can con-
tain considerable amounts of silica (28–34 % SiO2). 
Struvite can have a liming effect and hence may be 
suitable for acidic soils [30, 31].

Pollutant contents

Toxic element content, speciation and 
bioavailability

Toxic element ions can be incorporated into the 
struvite crystalline network by nucleation and also 
during the crystal growth process [31]. The current 
database on contents of (potentially) toxic elements 
like arsenic (As), cadmium (Cd), chromium (Cr), 
lead (Pb), molybdenum (Mo), nickel (Ni), copper 
(Cu) and zinc (Zn) is very limited and relies on data
from individual waste water treatment plants. There is a lack of data assessing the transfer rates to precipitation products of these elements depending on the characteristics of the source materials. The available data indicates that traces of these elements are included in the precipitation products (Table 2), originating from elements dissolved in the aqueous phase; however, in all cases concentrations are below critical values according to the European fertilizer ordinance [32]. In comparison, the variability in concentration of trace elements in stabilized sewage sludge and rock P is significant (Table 2) and reported values in precipitation products are always lower than the values reported in rock P or sludge.

The heavy metal – nutrient relationship (HMN) is an index for the (potentially) toxic element load (weighted according to their respective potential environmental impact) related to the (plant) nutritional value of the fertilizers, with higher values indicative of a higher toxic element load relative to the benefit attainable by the fertilizer use [33]. The HMN indices indicate very low levels of contaminants in the precipitation products in comparison to stabilized sewage sludge or phosphate rock from sedimentary deposits (Table 2). The HMN indices of the precipitation products are also well below average values found in bio-waste composts (0.69), and green-waste composts (0.72). The values for precipitates are comparable to values found for solid cattle manure (0.10) and slurry (0.07) on organic farms [34].

**Persistent organic pollutants**

We have found only a few studies which evaluate the presence of persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in struvite precipitated from sewage treatment plants. No PCB was found in struvite precipitated from the liquid effluent of a sewage sludge anaerobic digester [37] and very low levels of POP were found in struvites obtained via the "Stuttgarter process" [37]. Also POP contents of the already in the market available struvite fertilizer "Berliner Pflanze" from the treatment plant "Walßmannsdorf" is low with contents of AOX of 55 mg/kg and of PAHs 7.2 mg/kg [34]. It is likely that these micro-pollutants were concentrated and incinerated with the remaining filter cake.

**Xenobiotics**

It was found that more than 98% of hormones as well as pharmaceuticals remained in solution during precipitation [38]. Only very small amounts of pharmaceuticals were found attached to the struvite crystals, and could even be removed by rinsing the crystals after filtration.

**Hygienic aspects**

Human pathogens including bacteria and enteric viruses can infect and replicate in the gastrointestinal tract of humans [39] and are excreted and transported to waste water treatment plants with the fecal matter. During the standard stabilization treatment (Figure 1), bacteria are reduced in the sewage sludge through a thermophilic (50–55°C) anaerobic digestion. This inactivates coliforms and Salmonella species within a few hours (exception: S. senftenberg). However, some pathogens are able to survive the treatment in an anaerobic digester (e.g., Campylobacter jejuni, Clostridia, Bacillus-species, BSE), e.g., by forming resistant spores [40, 41, 42, 43, 44, 45].

Decrey [46] investigated the behavior of different human pathogens and viruses during precipitation and drying of struvite and found retained microorganisms in the struvite. Pathogen inactivation was dependent on temperature and humidity during drying and the length of the drying period. Overall, there seem to be promising procedures to reduce human pathogens and viruses in precipitation products, but there is as yet little data available and further research is needed. In particular, there are no data on how the source and previous treatment of the substrate influences the hygienic status of the P fertilizer, as well as the effects of duration of precipitate storage before field application.

**Other aspects**

**Available energy inputs data**

P recovery by precipitation of struvite involves considerably lower energy inputs, compared to P-recovery from sludge incineration by the ASH DEC© procedure [5]. However, P recovery procedures based on P precipitation are limited to recovery of the dissolved (depending on the setup also the dissolvable) fraction of P, and not the organically bound P, meaning that under practical conditions only about 10 to 70% of the total P load entering a sewage treatment plant is recovered using this method, whereas ash based procedures allow the recovery of most of the P.

**Life Cycle Assessment of sewage disposal**

So far, Life Cycle Assessment (LCA) data are scarce for the specific processes of sewage sludge disposal combined with P-recovery through struvite or Ca-P precipitation.

**Emissions of the production process and field application**

Data on emissions during the production process are very scarce. Assessments indicate that the GHG emissions by recovering P from sewage sludge by incineration (Ash Dec process) are higher compared to P recovery by struvite precipitation, due to the required energy input for incineration [5].
Provisional assessment of the suitability for use in Organic Farming

According to EU legislation, the application of struvite and Ca-phosphates recovered from waste water or sewage sludge are not allowed in organic farming [47]. Recent technological developments may have come far enough for a careful re-consideration of this legislation. Such a re-consideration should include at least five aspects: (i) the share of nutrients recovered by the process, (ii) the processes and additives applied to obtain the fertilizer, (iii) their potential environmental impact, (iv) the mode of action of the fertilizer in the soil and fertilizing efficiency, and (v) potential long-term effects on soil contamination and environmental pollution.

The use of precipitated struvite or Ca-phosphates is one means to close the current gap in the organic food cycle and hence meets the basic principle of align well with organic principles. Furthermore, the low levels of contaminants in precipitation products suggest a low pollution risk. However, the particularly high load of chemicals consumed in some of the production processes to dissolve phosphates as a basis for subsequent struvite crystallization does not align well with organic principles. Furthermore, the efficiency in terms of nutrient recovery rate for P is much lower compared to ash based processes (but higher for N and S). A further weakness of the available P recovery processes based on precipitation is the treatment of the remaining sludge, which is low in P and often enriched in toxic elements.

One major challenge for future discussions about the suitability of the available recycling options are the elaboration of criteria and a ranking of criteria for their evaluation. For example, what is more important for the assessment of suitability of any P recovery procedure for organic farming, the effectiveness in terms of % recovered P, the source (e.g. finite, recycled), the environmental impacts (e.g. life cycle analyses of the entire process per unit product) or particular properties of the fertilizer regarding the water solubility, the speed of action or nutrient release in the soil.

Conclusions

The use of precipitation processes is a promising option to recycle a substantial part of P from the urban food chain back to the land using a relatively simple procedure. In this regard, struvite and Ca-P products recovered from sewage sludge, urine or waste water meet basic organic principles. However, a more detailed assessment of the chemicals consumed to produce struvite and Ca-P from these waste products needs to be conducted before a conclusive recommendation can be made. The potential contamination with pathogens has to be a matter of further research. The precipitation processes are limited to recovering the dissolved ortho-P (and in processes with acidification, the re-dissolved phosphates) and not the total P. One option for a more efficient P recovery could be to combine these procedures with an incineration step where insoluble P as well as toxic elements can be separated and recovered.

References


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