



Australian Government
Department of Agriculture



Fast-tracking new struvite separation technology adoption – industry feasibility review of the technology

Final Report
APL Project: 2016/2248

June 2017

Department of Agriculture and Fisheries

Ms Jaye Hill, Dr Christopher Pratt and Adjunct Prof. Matthew Redding
203 Tor Street
Toowoomba QLD 4350



Disclaimer: The opinions, advice and information contained in this publication have not been provided at the request of any person but are offered by Australian Pork Limited (APL) solely for informational purposes. While APL has no reason to believe that the information contained in this publication is inaccurate, APL is unable to guarantee the accuracy of the information and, subject to any terms implied by law which cannot be excluded, accepts no responsibility for loss suffered as a result of any party's reliance on the accuracy or currency of the content of this publication. The information contained in this publication should not be relied upon for any purpose, including as a substitute for professional advice. Nothing within the publication constitutes an express or implied warranty, or representation, with respect to the accuracy or currency of the publication, any future matter or as to the value of or demand for any good.

Acknowledgements

This project is supported by funding from Australian Pork Limited and the Department of Agriculture and Fisheries.

Executive Summary

Globally the demand for fertilizers is increasing. However, mineral phosphorus (P) fertilizer reserves are sourced from a finite resource. Australia is the world's fifth largest consumer of P fertilizers. Agricultural manures, such as piggery effluent, can help meet some of these demands as manures contain large quantities of P and Nitrogen (N). Currently manure use as a fertilizer is limited by high transportation costs and its point source discharge can lead to environmental concerns. The production of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) from these manure streams has the potential to concentrate the nutrients into a stable fertilizer compound. Struvite extraction techniques are available for piggery effluent but only a small proportion (10-20%) of total phosphorus (TP) in piggery effluent is in a form suitable for struvite precipitation. Still, there is scope to optimise the proportion of available P in piggery effluent and thus real potential to elevate struvite as a more concentrated and efficient P fertilizer source than sludge, which is currently the industry's most P-enriched waste material.

Numerous countries, including the United Kingdom, Japan, Canada and the USA already market struvite as an environmentally friendly green product such as "Green MAP II". Studies have demonstrated struvite is potentially effective as a long-term slow-release fertilizer product. However, there are several gaps in our understanding of struvite's efficacy as a fertilizer, particularly concerning struvite performance in alkaline conditions. This review has determined that even though struvite solubility rapidly declines in alkaline conditions, there is the potential for plants to access struvite P at elevated pH (7.5) via environmental and microbial processes. However, testing at alkaline conditions is needed to verify this. There is also the potential for the use of struvite to improve farming operations within Australia. Its slow release in the soil could be of benefit in regions where P and N leaching is of concern such as agricultural lands surrounding the Great Barrier Reef Marine Park. Additionally, struvite's ability to increase soil pH may be of benefit for regions in Australia currently facing acidification problems – in these cases application of struvite could achieve the twinned benefit of delivering P to plants as well as alleviating, at least to some extent, soil acidity. Testing in this area is recommended.

Within Australia it is currently unclear how a material such as struvite would sit within the regulatory framework when examining its application to soils. In the case of struvite from domestic wastewater treatment plants (WWTP) unless the Department of Primary Industries classify the product as a 'fertilizer' it is likely that the struvite will have to meet 'Grade A Biosolid stabilization legislation' before it is allowed to be used without restriction. However, the fate of struvite from piggery treatment systems is less clear as they more likely to be regulated under State jurisdiction. Further clarification would be required at a state level, prior to its widespread application to soils.

Globally there are still significant gaps and inconsistencies in the literature regarding the economics of struvite formation from wastewater sources at full-scale production. This is particularly true for piggery waste with no feasibility studies identified in our review. However, economic feasibility studies for WWTP within Australia have estimated struvite production costs at approximately US\$613-1500/Tonne. This is substantially more than the US\$320/Tonne price of conventional Mono-Ammonium Phosphate (MAP) fertilizers. This price difference can mostly be attributed to the lack of environmental offset or "avoided costs" within Australia, which makes struvite production more expensive than in countries such as the USA or Japan where P disposal is closely regulated. These high costs within Australia currently limit struvite use, particularly at broad scale; however, it could be marketed as a boutique, environmentally friendly fertilizer until economic feasibility improves. An analysis of the economic and social determinants of adoption of the technology of struvite recovery and fertilizer development, especially as it relates to the Australian Pork Industry, is recommended.

Table of Contents

Acknowledgements 2

Executive Summary 3

1. Introduction 7

2. Objectives of the Research Project 8

3. Recovery of struvite from piggery effluent 9

4. Agronomics 12

4.1 General Agronomic Considerations and Preliminary Trials 12

5. Economics 17

6. Implications and Recommendations 19

7. Conclusions 20

8. Literature Cited 21

List of Tables

| | |
|---|----|
| Table 1: Summary of chemical partitioning in piggery effluent (Tucker, 2015). VS = volatile solids; TS = total solids | 9 |
| Table 2: Review of wastewater use in the recovery of nutrients from agricultural waste adapted from Kumar and Pal (2015). TAN = Total Ammonia Nitrogen OP = orthophosphate | 11 |
| Table 3: Chemical composition of struvite deposits and commercial fertilizers used in agricultural tests (Ryu and Lee, 2016) | 13 |
| Table 4: Concentration of heavy metals in soil, commercial fertilizers and struvite (Ryu and Lee, 2016) | 15 |
| Table 5: Chemical characteristics of the struvite extracted from Gatton and Grantham piggery wastewater, extracted using Magnesium chloride ($MgCl_2$) and Magnesium hydroxide ($Mg(OH)_2$) from (Mehta, 2015) alongside New South Wales Department of Environment and Conservation (NSW DEC) classes of biosolids based on contaminants (Burgess et al., 2015) | 16 |
| Table 6: Summary of struvite performance in agronomic trials. Not all trials applied appropriate agronomic practices (e.g. basal nutrient application for non-trial nutrients) | |
| Error! Bookmark not defined. | |
| Table 7: P use by sector (source: (Burgess et al., 2015) | 17 |

List of Figures

Figure 1: Scanning microscopy image of a struvite crystal produced from different inflow sources: A) synthetic struvite tight aggregates of fine crystals (DAF unpublished work); the peaks on the right show energy-dispersive spectroscopy analysis of a location on the crystal surface; B) Piggery effluent dispersive spectroscopy analysis of a location on the crystal surface, revealing a strong carbon peak highlighted in green (DAF unpublished work); C) Mineral fertilizer industry wastewater (Matynia et al., 2013); D) Brisbane City Council wastewater-derived struvite (Münch and Barr, 2001). 12

Figure 2: A) The effects of solution pH on 2.4 mm struvite granule dissolution. Changes in solution P concentration over time B) Organic acid promotion of struvite P dissolution and uptake, the effect of 1 μ M oxalic acid, malic acid, acetic acid, or citric acid on struvite P dissolution (Talboys et al., 2016). 14

Figure 3: Soil pH changes: T_0 = control, T_1 = MAP based on 30 kg P ha⁻¹, T_2 = FSP based on 30 kg P ha⁻¹+ urea equivalent to N of MAP applied in T_1 , T_3 = MAP based on 40 kg P ha⁻¹, T_4 = FSP based on 40 kg P ha⁻¹+ urea equivalent to N of MAP applied in T_3 (Rahman et al., 2011) 15

Figure 4: Relative fertilizer efficiency of PR and recycled P products determined in a 2-year pot experiment on two different soils. The increase in P uptake by maize due to TSP was set to 100% (Cabeza et al., 2011)

Error! Bookmark not defined.

I. Introduction

Wastewater from agricultural and domestic treatment processes contains high amounts of nitrogen (N) and phosphorus (P). Inappropriate discharge of this wastewater can lead to environmental concerns such as eutrophication (Carpenter *et al.*, 1998; Smith *et al.*, 1999). However, these nutrient-rich waste streams are being increasingly recognised as valuable sources of fertilizer. Globally mineral P fertilizers are manufactured from finite reserves of phosphate rock (PR) which are steadily being depleted (Cordell *et al.*, 2009; Elser *et al.*, 2014). This is occurring in an environment where world demand for total fertilizer nutrients is increasing. The FAO (2016) predicts that the demand for N and P will grow annually by a factor of 1.2 and 2.0, respectively, during the period from 2015 to 2019. There is rising concern over the affordability of fertilizers and associated potential to threaten future food security, especially given PR reserves are restricted to very few countries (Cordell and Neset, 2014; Elser *et al.*, 2014).

Piggery effluent contains high concentrations of P and N, primarily due to diets with high indigestible components being fed to the animals. For example, a substantial proportion of P in pig feed is in the form of phytate and this compound is not thought to be readily digestible for monogastric livestock such as pigs. Pigs have a very low phytase activity within their digestive tract (Humer *et al.*, 2015) and consequently can only digest 14% of the P available within corn and 23-31% of the P in soybean meal (Baker, 2000) – ingredients that form a large proportion of pig diets. Subsequently, the undigested phytate P is excreted to wastewater systems. Similarly, approximately 20% of the total N ingested by pigs is excreted in faeces predominantly in the form of bacterial proteins, while 50% is excreted in urine as urea (Canh *et al.*, 1998). As a result dietary protein content has a major effect on the quantity of ammonium within piggery effluent. The large quantity of P and N excreted by pigs makes piggery effluent a promising candidate for fertilizer extraction.

Given the growing strain on fertilizer supply and demand, technologies that attempt to close the P and N loop are becoming increasingly important. Although waste streams are reasonably nutrient-rich, the haulage cost of wastewaters to agricultural lands can often limit their use. Additional concerns such as hazardous organic compounds, pathogens, high metal content and odour can also limit waste application (Cabeza *et al.*, 2011). The extraction and concentration of nutrients therefore becomes an important consideration, with one such method being the precipitation of the mineral struvite.

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is a mineral consisting of equal moles of ammonium, phosphorus and magnesium as well as six water molecules. On an elemental basis, struvite contains 13% P, 6% N and 10% Mg making it reasonably nutrient-dense compared with conventional fertilizer products (Rahman *et al.*, 2014). Struvite came to interest largely due to its scalelike formations on pipes and pumps within wastewater treatment systems, such as anaerobic digesters (Suzuki *et al.*, 2007). While these precipitates are largely unwanted, the controlled formulation of struvite has been proposed as a method of resource recovery for both N and P (Kumar and Pal, 2015).

The recovery of struvite from different wastewater treatment systems has been widely investigated (Regy *et al.*, 2002; Adnan *et al.*, 2003; Suzuki *et al.*, 2007; Zhang *et al.*, 2009; Liu *et al.*, 2011b; Matynia *et al.*, 2013). However, there has been limited work undertaken focusing on its performance as a fertilizer compared against conventional products. This document reviews available literature to assess the industry feasibility of piggery-derived struvite as a viable nutrient source in the Australian agricultural context.

2. Objectives of the Research Project

To undertake an industry feasibility review of struvite recovery and adoption for the Australian pork industry. The review will incorporate the latest estimates of agronomic benefits from struvite recovery in order to provide the industry with a basis on which to pursue any potential future work in this area.

3. Recovery of struvite from piggery effluent

There has been a wealth of studies examining and optimising techniques for extracting struvite from a range of wastewaters including: landfill leachate (Li and Zhao, 2003); poultry wastewater (Yetilmezsoy and Sapci-Zengin, 2009a); anaerobically digested dairy waste (Tao *et al.*, 2016); domestic wastewater (Huang *et al.*, 2015); and piggery effluent (Suzuki *et al.*, 2005; Song *et al.*, 2011; Mehta, 2015). Although not the focus of this review, a brief understanding of these recovery processes is needed in order to gain a complete picture of the feasibility of piggery-derived struvite as a viable and competitive fertilizer product. Broadly, key criteria for efficient struvite recovery from any stream involves: sufficient molar ratios of Mg, N and P (i.e., 1:1:1); alkaline conditions (i.e., pH>8); and suitable seed sites to initiate the process of crystal nucleation.

In raw piggery wastewater typical NH_4^+ , Mg^{2+} and PO_4^{3-} ratios do not meet the optimum 1:1:1 molar ratio required for struvite formation (Song *et al.*, 2011). Additionally, for piggery effluent a large proportion of P and Mg exist in insoluble forms (see Table 1: Summary of chemical partitioning in piggery effluent (Tucker, 2015).

). In general, piggery wastewater contains more than $20 \times \text{NH}_4\text{-N}$ than orthophosphate ($\text{PO}_4^{3-}\text{-P}$) (Liu *et al.*, 2011a). This presents a challenge for struvite production that can be addressed either through: the addition of the limiting constituents – Mg (such as MgCl_2) and/or P ($\text{NaPO}_4 \cdot 12\text{H}_2\text{O}$) (Mehta, 2015); or by dissolving the solid P fraction via crystallization (Suzuki *et al.*, 2007; Liu *et al.*, 2011b), chemical processes (Huang *et al.*, 2016b) or microbial pathways (Manas *et al.*, 2012).

Table 1: Summary of chemical partitioning in piggery effluent (Tucker, 2015).

| | Floating | Settled | Suspended | Dissolved |
|-----------|----------|---------|-----------|-----------|
| N | 1-10% | 15-30% | 10-20% | 50-70% |
| P | 1-10% | 50-70% | 20-30% | 10-20% |
| VS | 1-10% | 55-75% | 5-15% | 10-20% |
| TS | 1-10% | 55-75% | 5-15% | 10-25% |

VS = volatile solids; TS = total solids

Along with ion availability, alkaline conditions are required for struvite formation. Doyle *et al.* (2002) found that altering the pH of sludge liquor from 7.5 to 8.5 increased precipitation potential from 116 mg L^{-1} to over 200 mg L^{-1} . Kumar and Pal (2015) note that struvite precipitation can be restricted if the waste stream pH is too high (>10.5). This results in the precipitation process being hampered by the volatilisation of free ammonia (NH_3) and associated loss of NH_4^+ ions necessary for crystallisation. Additionally, the presence of competing cations, notably Ca^{2+} , can limit the amount of struvite formed in wastewater through promoting mineralisation of other insoluble compounds (Kumar and Pal, 2015). Indeed, piggery effluent might even prove more amenable to efficient struvite precipitation compared with other waste streams given the relatively high proportion of ammonium, urea and uretic bacteria in piggery manure (Dai and Karring, 2014). These constituents can result in effluent streams with naturally high pH, hence eliminating costs associated with chemical dosing (NaOH) or aeration which are typically employed to modify pH. Zhang *et al.* (2012) note that the high concentration of NH_4^+ in swine wastewater hampers the anaerobic digestion process. The authors suggest that the struvite formation could be used as a precursor to anaerobic digestion to reduce the inhibitory effect of NH_3 . However, care would need to be taken with this approach, as the optimum pH for anaerobic digestion is 6.5-7.5 (Svoboda, 2003).

Suzuki *et al.* (2007) tested the logistics of a struvite seed and recovery device for treating swine wastewater. The effluent was screened through a 1.5 mm sieve and the struvite recovery device incorporated an aeration component which was able to successfully maintain the effluent pH in the optimal zone (8.5) for struvite precipitation. The pH is maintained at this level by stripping CO_2 from

the stream. Following addition of Mg – in this case MgCl_2 (bittern) – the authors reported a Maximum struvite yield of 171 g m^{-3} wastewater. This yield corresponded to a recovery of approximately 15% of the TP in the wastewater, indicating potential for further optimisation. Mehta (2016) also engineered a device to extract struvite from piggery effluent. This investigation also reported successful struvite recovery although it was noted that the process is optimal when solids concentrations are <1000 ppm. Moreover, the addition of extra P as well as Mg was needed which would incur additional input costs at full-scale. Encouragingly though, the pH of the effluent stream was sufficiently alkaline (>7.8) to avoid the need for aeration to increase pH.

Çelen *et al.* (2007) produced a useful model for predicting the expected struvite recovery from piggery effluent through input parameters including: pH; N, P, Mg and competing cation concentrations; and alkalinity. In verifying the model the authors found Mg input to be the major factor limiting successful struvite recovery. Interestingly, from a practical perspective, another study focusing on the impacts of parameter inputs on struvite recovery from piggery effluent revealed that a crystal seeding step was not necessary for effective struvite precipitation (Burns *et al.*, 2003).

Mineral precipitation from the liquid effluent stream is not the only way to produce struvite from piggery wastes. Ren *et al.* (2010) assessed the prospects of extracting struvite from solid composted pig litter, using magnesium hydroxide and phosphoric acid to stimulate struvite crystallisation. These authors reported successful struvite formation in the compost, although the acidity of the phosphoric acid did inhibit composting processes in some treatments (Ren *et al.*, 2010).

The logistics of struvite recovery from piggery effluent suggest that successful precipitation is achievable given that piggery effluents present similar composition to other wastewater types – for which economically viable struvite recovery has been demonstrated (Kumar and Pal, 2015). However, the fact that a large proportion of TP and Mg in piggery effluent is in the solid fraction and quickly settles out of solution limits struvite potential production. The main limitation to struvite production from piggery effluent, as for most streams, appears to be the insufficient concentrations of Mg. Kumar and Pal (2015) report that Mg addition accounts for approximately 75% of input costs for intended struvite recovery across all waste streams. For pig farms, this could be overcome by using novel Mg feedstock sources such as mineral-rich aquifer water or by adding compounds that are cheaper than Mg chemicals, such as ferric chloride, which can stimulate solubility of the stream's existing Mg compounds (Laridi *et al.*, 2005). Any other approaches that can optimise the partitioning of P in the liquid stream relative to the solid/sludge fraction could potentially further improve the prospects for efficient struvite recovery from piggery effluent streams.

However, while struvite precipitation from piggery effluent is possible, reported production volumes across different piggeries are highly variable and care needs to be taken when interpreting extraction efficiencies. Factors such as what portion of the wastewater treatment stream is being investigated (raw manures, treated effluent, removed sediments) can have large impacts on the total P concentration considered and subsequent recovery rates. Le Corre *et al.* (2009), for example, reported that up to 70% of P in effluent streams can be recovered as struvite, although it is unclear whether this relates solely to the liquid phase P content or the P concentration of the combined solid + liquid fractions. Additionally, different studies place different emphasis on their objectives for struvite recovery. For example, in some cases N removal is the primary objective and P addition is required. Table 2: Review of wastewater use in the recovery of nutrients from agricultural waste adapted from Kumar and Pal (2015).

below reviews reported struvite recovery rates and operational conditions for piggery systems. It should be noted that within some studies it is unclear if P removal from the wastewater stream directly correlates with struvite production. For example, Song *et al.* (2011) note that 85% of total P was recovered from anaerobically digested wastewater; however, of that only 35% was recovered as struvite. Other studies focused on the potential environmental benefits from P removal, yet present overall P removal with no calculations provided for struvite recovery (see below).

Table 2: Review of wastewater use in the recovery of nutrients from agricultural waste adapted from Kumar and Pal (2015).

| Wastewater | Removal | Molar ratio used | Removal efficiency | Reference |
|---------------------------------|--------------|-----------------------|--|-------------------------------|
| Swine WW | Both P and K | 1.79 (Mg/P) | Anaerobically digested wastewater 85 % (TP) removed 40-90 % (N) 35% recovery as struvite | Song et al. (2011) |
| Swine WW | Both N and P | 1:1:1.2 (P/Mg/N) | Raw effluent Added P NaPO ₄ .12H ₂ O 96 % (OP) 87 % (N) | Zhang et al. (2012) |
| Swine WW Screened | Both N and P | 08:1 (Mg/P) | 65 % (TP) 67 % (TN) P redissolved in acid | Liu et al. (2011a, b) |
| Swine WW Screened | Both N and P | Aeration | No added P | Suzuki et al. (2005) |
| Swine WW | Only P | 1:1 (Mg/P) | No added P 93 % (OP) and 32% NH ₄ -N | Rahman et al. (2011) |
| Swine WW | Both N and P | 2M struvite dissolved | 79 % (OP) and 53 % (N) | Liu et al. (2011a, b) |
| Swine WW Screened | Only P | – | no added P 30% added MgCl ₂ 171 g.m ⁻³ struvite screened effluent 18-49% P recovered as struvite | Suzuki et al. (2007) |
| Swine WW | Only P | – | 82 % (TP) only 4.6-27% of TP struvite remained settled out of solution. Microbial fuel cells other P sediments. | (Ichihashi and Hirooka, 2012) |
| Swine WW | Only P | 1.6:1 (Mg/P) | 91 % (OP) | (Burns et al., 2001) |
| Swine Ww Holding Pond-Untreated | Only P | | NaOH adjusted pH 55% P(OP), 36% NH ₄ ⁺ Mg ²⁺ :PO ₄ ³⁻ 2:1 98% P(OP), 46% NH ₄ ⁺ | (Çelen et al., 2007) |
| Swine WW Filtered At 0.45µm | P and N | | 93% removal of TAN and OP Reuses struvite a P source for TAN removal. | (Huang et al., 2016b) |
| Swine WW Filtered At 0.45µm | TAN | | Adds Mg ³ (PO ₄) ² for TAN removal 78% | (Huang et al., 2016a) |
| Swine WW | Ammoniacal N | | Adds P and Mg source Removes 70% Ammoniacal N | (Mehta, 2015) |

*TAN = Total Ammonia Nitrogen OP = orthophosphate

The precipitation of struvite from piggery effluent streams is certainly achievable, as evidenced by a long list of case studies. However, the process is far from simple, and in most experiences, additional inputs appear to be required. In most cases, struvite formation is nowhere near able to harness the total P content of the effluent stream. Still, there is scope to optimise struvite recovery from piggery effluent and the real potential to elevate this mineral as a more concentrated and efficient P fertiliser source than sludge, which is currently the industry's most P-enriched waste material.

4. Agronomics

4.1 General Agronomic Considerations and Preliminary Trials

Pure or synthetic struvite contains approximately 12.65% P while struvite recovered from waste streams is characterised by P concentrations ranging from 6-12% P (Johnston and Richards, 2003; Cabeza *et al.*, 2011). Struvite crystal structure and size can vary depending on formation conditions (Zhang *et al.*, 2009) and various morphology types have been recorded: as star-like particles (Regy *et al.*, 2002; Zhang *et al.*, 2009); tight aggregates of fine crystals (Adnan *et al.*, 2003); irregular coarse structures (Zhang *et al.*, 2009; Rahman *et al.*, 2014); as well as elongated structures (Le Corre *et al.*, 2005; Matynia *et al.*, 2013). Struvite crystals have been documented ranging from 15µm (Zhang *et al.*, 2009) to 3.5mm (Adnan *et al.*, 2003) in size. **Error! Reference source not found.** below demonstrates the variability in struvite morphology.

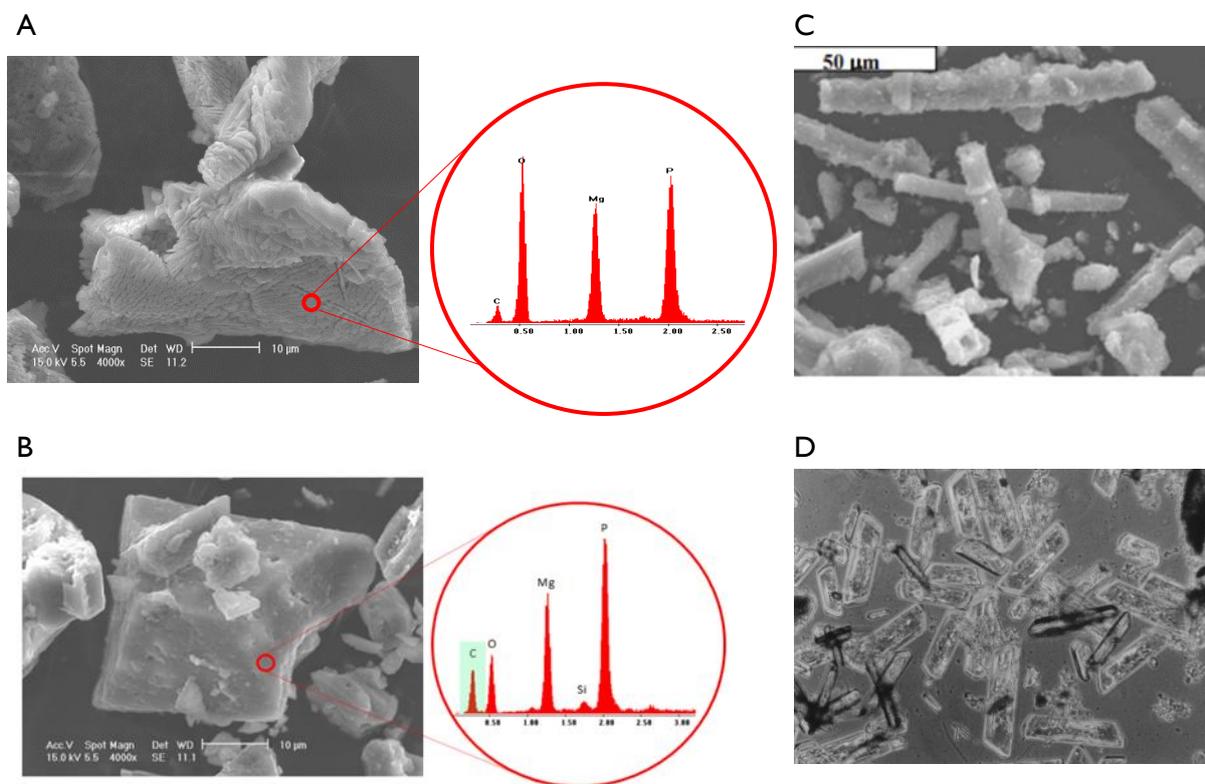


Figure 1: Scanning microscopy image of a struvite crystal produced from different inflow sources: A) synthetic struvite tight aggregates of fine crystals (DAF unpublished work); the peaks on the right show energy-dispersive spectroscopy analysis of a location on the crystal surface; B) Piggery effluent dispersive spectroscopy analysis of a location on the crystal surface, revealing a strong carbon peak highlighted in green (DAF unpublished work); C) Mineral fertilizer industry wastewater (Matynia *et al.*, 2013); D) Brisbane City Council wastewater-derived struvite (Münch and Barr, 2001).

The wastewater source, recovery and seeding technique can all alter the chemical composition and physical properties of struvite. Table 2: Review of wastewater use in the recovery of nutrients from agricultural waste adapted from Kumar and Pal (2015).

above summarises the different molar ratios of N:P:Mg found within struvites formed from a variety of piggery effluents (Kumar and Pal, 2015). In comparison to the synthetically made products, struvite from wastewater can also contain high levels of organic carbon, with 1.93% to 20% noted within some products (Achat *et al.*, 2014; Ryu and Lee, 2016). **Error! Reference source not found.** A and B above show a substantial peak for carbon in piggery struvite compared with a synthetically produced source. These compositional differences may affect the nutrient release profile of struvite in soil. For example, the application of piggery struvite to soils in incubation trials has been shown to increase soil microbiological activity compared with synthetically produced struvite, conventional fertilizer ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) or hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). Piggery-derived struvite increased soil respiration by 30% during the first three days post-application (Achat *et al.*, 2014) while synthetic sources did not significantly increase soil microbiology activity. Achat *et al.* (2014) note that soil microorganisms have the potential to solubilise any available Ca-P through acidification that might be present within the struvite compound contributing a positive role to P availability.

Table 3: Chemical composition of struvite deposits and commercial fertilizers used in agricultural tests (Ryu and Lee, 2016)

| Elements | Complex Fertilizer | Organic Fertilizer | Struvite |
|---|--------------------|--------------------|----------|
| N | 11 | 5.0 | 14.8 |
| O | n.m. | n.m. | 34.0 |
| Mg | 4 | 9.3 | 10.2 |
| Si | 14 | n.m. | n.m. |
| P | 6 | 0.4 | 15.6 |
| K | 6 | 0.9 | 2.0 |
| Ca | 20 | 13.3 | n.m. |
| B | 0.1 | n.m. | n.m. |
| B | n.m. | n.m. | 20.0 |
| Cl | n.m. | n.m. | 3.4 |
| Note: All indicated figures are based on weight percent (wt.) | | | |
| Note: In this table, compost was not included and its composition can be found in the text. | | | |
| n.m.: Not measured. | | | |

Typically, the solubility of pure struvite is low (0.23 g L^{-1}) compared with $\text{Ca}(\text{H}_2\text{PO}_4)_2$: (18 g L^{-1}) (Weast, 1970). This results in struvite being only slightly soluble in water i.e., 1-5% (Cabeza *et al.*, 2011). Plants dissolve P from the soil solutions and therefore to become an effective P fertilizer the material must be soluble within soil water solutions (Cabeza *et al.*, 2011). Despite this low solubility, studies have noted that struvite from wastewater is effective as a water-soluble fertilizer in slightly alkaline (approx. 7.5 pH), neutral and acidic soils (Johnston and Richards, 2003; Massey *et al.*, 2009; Cabeza *et al.*, 2011; Achat *et al.*, 2014). Data on availability at more alkaline conditions is scarce.

Given struvite's relatively low solubility at neutral to mildly alkaline conditions, concerns exist regarding its ability to effectively deliver nutrients, particularly P, to plants. In Australia, where vast tracts of agricultural land cover alkaline soils, this is a potential obstacle to struvite uptake as an effective fertilizer product. However, there are management practices as well as technical approaches that can be employed to overcome this limitation. Modifying soils with acid-generating chemicals is one such approach, although obviously balance is needed to minimise the negative impacts of soil acidification. In fact, many agricultural regions in Australia are already currently facing acidification problems – in these cases application of struvite could achieve the twinned benefit of delivering P to plants as well as alleviating, at least to some extent, soil acidity. It should also be noted that a variety of soil microbiota are capable of solubilising nutrient sources through supplying organic acids and other

active compounds to the soil rhizosphere. A considerable component of the bacterial group now recognised as ‘plant growth promoting rhizobacteria’ (PGPR) is capable of direct P solubilisation (Collavino *et al.*, 2010; Mander *et al.*, 2012). Indeed, many of these bacterial strains are being incorporated into new fertilizer formulations termed ‘biofertilizers’ (Malusá *et al.*, 2012). The development of these emerging fertilizers, in conjunction with increasing knowledge regarding native soil microbial dynamics, could pave a practical way forward to optimise nutrient availability from struvite fertilised soils.

Despite potential concerns regarding struvite solubility, Cabeza *et al.* (2011) note that the soil conditions seem to be generally effective in solubilising struvite, with wastewater-derived struvite increasing the P concentrations in soil solutions to similar levels achieved by Triple Super Phosphate (TSP) at neutral and acidic pH. Cabeza *et al.* (2011) conclude that solubility as measured in water does not accurately characterise P availability for plants. They note that many plants can create their own conditions to solubilise P. This finding was supported by Talboys *et al.* (2016) who noted that struvite solubility is greatly enhanced in the presence of organic acid anions such as oxalate, malate, acetate and citrate. These ions are known to play roles in mobilising P in soil profiles from compounds such as iron oxides (Jones *et al.*, 2003; Johnson and Loeppert, 2006). A solubility assessment undertaken by Talboys *et al.* (2016) showed a significant increase in both the rate of dissociation and the equilibrium P concentration when organic acids were used compared with solely adjusting the pH in water (**Error! Reference source not found.**). Massey *et al.* (2009), in an agronomic trial, examined struvite effectiveness in acidic (6.5) and slightly alkaline soils (7.6 adjusted with lime). The authors found that while the pH affected growth generally, all fertilizers performed similarly, indicating that struvite was equally available as TSP and rock phosphate under slightly alkaline conditions.

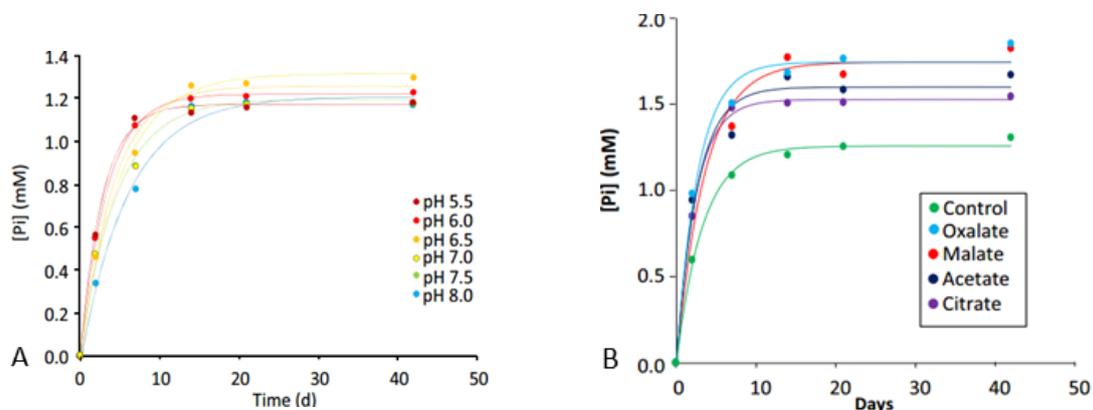


Figure 2: A) The effects of solution pH on 2.4 mm struvite granule dissolution. Changes in solution P concentration over time B) Organic acid promotion of struvite P dissolution and uptake, the effect of 1 μM oxalic acid, malic acid, acetic acid, or citric acid on struvite P dissolution (Talboys *et al.*, 2016).

Achat *et al.* (2014) found that P solubility of piggery struvites was low but their P mobility was similar to that of a commercial product – $\text{Ca}(\text{H}_2\text{PO}_4)_2$ – and, interestingly, higher than that of the reference (synthetic) struvites when examined using isotopic exchangeable phosphate ions. Again this may be related to the presence of organic materials in the piggery struvite.

Struvite has also been shown to effectively raise soil pH. As alluded to earlier, this could be of particular use in Australia which has a widespread soil acidification problem. Soil acidity affects approximately

50 million hectares or 50 % of Australia's agricultural land (NLWRA, 2001). Rahman *et al.* (2011) found that the pH of soil treated with struvite increased over a five-week period compared to soils treated with fused super phosphate and urea (**Error! Reference source not found.**). These compounds resulted in an initial pH increase but these levels then dropped to, or below, the starting soil pH.

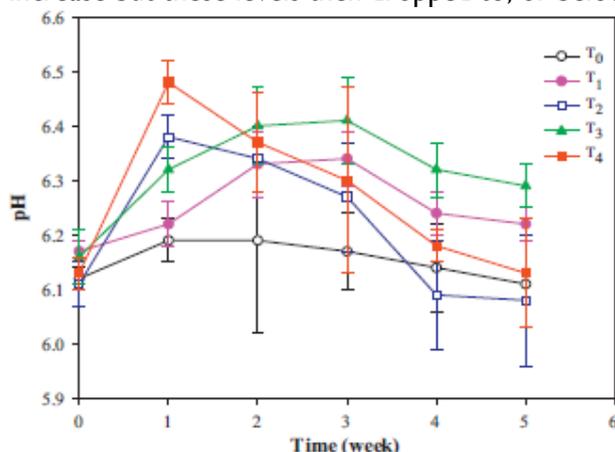


Figure 3: Soil pH changes: T₀ = control, T₁ = MAP based on 30 kg P ha⁻¹, T₂ = FSP based on 30 kg P ha⁻¹ + urea equivalent to N of MAP applied in T₁, T₃ = MAP based on 40 kg P ha⁻¹, T₄ = FSP based on 40 kg P ha⁻¹ + urea equivalent to N of MAP applied in T₃ (Rahman *et al.*, 2011)

Struvite may contain heavy metals depending upon the raw material used in its formation. Pb, Cd, Cr, Cu, Ni and Zn have all been detected within struvite produced from landfill leachate although they are noted to be below specified European directives for fertilizers (Cabeza *et al.*, 2011). In piggery struvite Cu, Cr and Zn concentrations have been recorded to be higher than in raw soil. However, Cr contents were lower than that of complex and organic fertilizers (Table 4: Concentration of heavy metals in soil, commercial fertilizers and struvite (Ryu and Lee, 2016)

| Heavy Metals (mg kg) | Soil | Complex Fertilizer | Organic Fertilizer | Compost Fertilizer | Struvite |
|----------------------|-------|--------------------|--------------------|--------------------|----------|
| Cd | 0.037 | 0.038 | 0.036 | 0.008 | 0.011 |
| Cu | 0.201 | 0.452 | 4.028 | 0.241 | 4.597 |
| As | n.d. | 0.156 | n.d. | n.d. | n.d. |
| Hg | n.d. | n.d. | n.d. | n.d. | n.d. |
| Pb | 0.599 | 0.005 | 0.157 | 0.022 | 0.034 |
| Cr ⁶⁺ | 0.216 | 3.064 | 0.398 | 0.098 | 0.341 |
| Zn | 1.750 | 2.711 | 8.843 | 0.139 | 14.9124 |
| Ni | 0.108 | 4.437 | 0.229 | 0.044 | 0.072 |

n.d.: Not detected.

(Ryu and Lee, 2016). Ryu and Lee (2016) also noted that lettuce tissue grown using piggery struvite did not have high levels of heavy metals compared with lettuce grown using other commercial fertilizers. It is useful to note that some of these metals such as Zn can be essential elements for plant growth when found in appropriate concentrations and therefore their presence in struvite does not automatically entail environmental or health concerns.

Table 4: Concentration of heavy metals in soil, commercial fertilizers and struvite (Ryu and Lee, 2016)

| Heavy Metals (mg kg) | Soil | Complex Fertilizer | Organic Fertilizer | Compost Fertilizer | Struvite |
|----------------------|-------|--------------------|--------------------|--------------------|----------|
| Cd | 0.037 | 0.038 | 0.036 | 0.008 | 0.011 |

| | | | | | |
|------------------|-------|-------|-------|-------|---------|
| Cu | 0.201 | 0.452 | 4.028 | 0.241 | 4.597 |
| As | n.d. | 0.156 | n.d. | n.d. | n.d. |
| Hg | n.d. | n.d. | n.d. | n.d. | n.d. |
| Pb | 0.599 | 0.005 | 0.157 | 0.022 | 0.034 |
| Cr ⁶⁺ | 0.216 | 3.064 | 0.398 | 0.098 | 0.341 |
| Zn | 1.750 | 2.711 | 8.843 | 0.139 | 14.9124 |
| Ni | 0,108 | 4.437 | 0.229 | 0.044 | 0.072 |

n.d.: Not detected.

Within Australia it is currently unclear how a material such as struvite would sit within the regulatory framework. Burgess *et al.* (2015) note that unless The Department of Primary Industries classify the product as a ‘fertilizer’ it is likely that struvite from a WWTP will have to meet ‘Grade A Biosolid stabilisation legislation’ before it is allowed to be used without restriction. Currently sludge from piggery ponds resides under differing state legislation regarding land application considerations. In Queensland it is not considered a ‘regulated waste’. However, it is unclear how waste-derived struvite will be regulated with regard to land application. Information in Ryu and Lee (2016) as well as analysis of the Australian struvite produced by Mehta (2015) indicates that the product should meet the ‘Grade A biosolid’ conditions for heavy metals, if required (see Table 5). However, site-specific analysis would be required at each production site.

Table 5: Chemical characteristics of the struvite extracted from Gatton and Grantham piggery wastewater, extracted using Magnesium chloride (MgCl₂) and Magnesium hydroxide (Mg(OH)₂) from (Mehta, 2015) alongside New South Wales Department of Environment and Conservation (NSW DEC) classes of biosolids based on contaminants (Burgess *et al.*, 2015)

| | Units | Gatton piggery | | Grantham Piggery | | NSW DEC Grade A biosolids |
|---|-------|-------------------|---------------------|-------------------|---------------------|---------------------------------|
| | | MgCl ₂ | Mg(OH) ₂ | MgCl ₂ | Mg(OH) ₂ | |
| P | % | 13.6 | 6.5 | 12.1 | 13.9 | |
| Mg | % | 12.2 | 28.4 | 11.6 | 14.9 | |
| N | % | 3.9 | 2.8 | 4.3 | 3.25 | |
| TC | % | 1.2 | 1.3 | 1 | - | |
| Ca | mg/g | 4.8 | 11.3 | 2.83 | 4.42 | |
| Cd | mg/g | 0.0 | 0.0 | 0.00 | 0.00 | 3 |
| Co | mg/g | 0.0 | 0.0 | 0.00 | 0.01 | |
| Cr | mg/g | 0.0 | 0.0 | 0.00 | 0.00 | 100 |
| Cu | mg/g | 0.1 | 0.0 | 0.01 | 0.01 | 100 |
| Fe | mg/g | 0.2 | 0.8 | 0.09 | 0.65 | |
| K | mg/g | 5.0 | 3.2 | 2.83 | 3.13 | |
| Water solubility | % | 2.9 | 1.1 | 5.1 | 2.7 | |
| Acid solubility 2% Citric acid | % | 89.4 | 81.7 | 91.1 | 86.5 | |
| Zinc | mg/g | | | | | 200 |
| Chlordane | | | | | | 0.02 |
| Dieldrin | | | | | | 0.02 |

5. Economics

Australia is the fifth largest consumer of P fertilizers in the world (Heffer, 2009), consuming about 400,000 tonnes of elemental P per year with its use divided between various agricultural sectors (Table 6: P use by sector (source: (Burgess et al., 2015)

) (Burgess et al., 2015). The potential total P from manures on Australian pig farms (based on sow populations of 267,000) is approximately 15,000 tonnes; however, only 1500-3000 tonnes of the available TP will be in soluble forms, such as orthophosphates, for immediate struvite formation. Assuming an 85% recovery rate of struvite from orthophosphates, the Australian pig industry has the potential to produce 10,000-20,000 tonnes of struvite. While this is a substantial quantity of potential P for Australian farms, the financial viability of obtaining the product needs to be critically evaluated.

Table 6: P use by sector (source: (Burgess et al., 2015)

| Agricultural Activity | % P fertilizer use |
|--|---------------------------|
| broad-acre cropping | 55 to 60% |
| pastures (beef, sheep and dairy) | 25% |
| sugar cane | 10% |
| horticulture (trees and vines, vegetables and flowers) | 15% |

Globally there are still significant gaps and inconsistencies in the literature regarding the economics of struvite formation from wastewater sources, particularly at full-scale production (Yetilmezsoy et al., 2017). This is particularly true for piggery waste, for which no studies of economic feasibility were identified. It should be noted, however, that Suzuki et al. (2007) ran a struvite recovery reactor using screened piggery effluent for 3.5 years, and while no figures on economic viability were provided, the authors note that a crystallization reactor integrated into the early stages of the wastewater treatment system on this site performed well over that time.

Molinos-Senante et al. (2011) note that in most cases studies pertaining to wastewater treatment, environmental regulation plays a major role in determining the economic viability of struvite production. Strict limits on the amount of P that can be released into the environment provides considerable financial incentives for operations to invest in P management technologies (Jia et al., 2017) and was the driving factor for the work by Suzuki et al. (2007). In Australia, P regulations either from point source discharges from farms or from fertilizers can vary depending upon state legislation. Generally fertilizer application is not strictly controlled. However, legislation such as the *Great Barrier Reef Marine Park Protection Amendment Act 2009* is able to limit P use in regions where environmental effects have been identified (Burgess et al., 2015).

The paucity of available cost benefit analyses makes it difficult to put a precise price on struvite, with reported values ranging from €208-€6100/T (Yetilmezsoy *et al.*, 2017). A review of the Oxley Creek wastewater treatment plant in Brisbane concluded that operating the struvite extraction plant at 55 Ml/d of sewage could range from a financial loss of \$13,000/yr to a profit of \$149,000/yr. This variability was largely dependent on the cost of magnesium added, the cost of struvite sold as well as the quantity of struvite recovered (Münch and Barr, 2001). Münch and Barr (2001) thought it would be possible for the recovered struvite to sell at AU\$300-500/T (US\$198-330T) with its most likely end product being potting mix or a commodity fertilizer. In 2001 fertilizer products such as DAP were valued at \$300/T. Today the current market value for monoammonium P as a broad acre product is AU\$430 (US\$320) (KochFertiliserTM, 2017). Jia *et al.* (2017) examined struvite recovery from another wastewater treatment system in South Australia in a more recent study. They predicted that struvite would need to be sold above US\$613/T and US\$685/T in order to mitigate the cost of utilising MgCl₂, NaOH and KH₂PO₄ to remove either P or N, respectively, depending upon the ion of interest (Jia *et al.*, 2017). A similar 2017 study undertaken in a WWTP in Turkey estimated that in order to cover operating costs only, the sale price of struvite would need to net €482/T (US\$545/T) with €560/T (US\$630/T) to cover a payback period of six years (Yetilmezsoy *et al.*, 2017). Burgess *et al.* (2015) examined two WWTPs in Australia and found that struvite would need to be marketed at AU\$1150-2000/T (US\$870-1500/T) in order to meet Net Present Value. They note that the lack of environmental offset or 'avoided costs' within Australia makes struvite production significantly more expensive than in countries such as the USA or Japan where P disposal is closely regulated.

It may be possible within some countries to improve struvite production efficiencies with larger economies of scale. Ideas such as Centralised Struvite Production systems might offer a solution. This would operate, similar to Centralised Anaerobic Digesters in Denmark, UK and America, where effluent for a range of industrial and agricultural processes are combined for power generation. However, these types of schemes have in the past been deemed unfeasible for Australia. This is generally attributed to the high transport costs to reach treatment sites as well as a relatively low population density (Poad and McGahan, 2010). It would be interesting to see how the addition of another valued product at the front end of treatment would alter the overall feasibility of such endeavours.

The high cost of production within Australia limits struvites potential use. Burgess *et al.* (2015) note that, as in the USA, struvite may find application in Australia's higher priced retail markets as a sustainable product. However, use as a broad scale fertilizer appears to be unviable at this stage. While there are concerns in Australia regarding the economic viability of struvite from WWTPs it should be noted that no cost benefit analyses have been identified which have specifically appraised struvite recovery and use pertaining to the Australian pork production context.

6. Implications and Recommendations

Several researchers and practitioners have assessed various aspects of struvite recovery from wastewater and its subsequent application as a nutrient source. Nonetheless, there are still several gaps in knowledge that need to be addressed in order to develop a satisfactory understanding of the efficacy of extracting struvite from waste streams and applying it as a fertilizer in agricultural settings. When focusing specifically on the context of Australia's piggery industry, a few critical aspects emerge as requiring attention before broad assessments of technical viability can be made. First, **a realistic appraisal of effluent P availability for struvite crystallisation needs to be conducted.** The current picture is that very little P excreted from pigs is available to participate in struvite precipitation, with most being tied up in complex forms in the sludge. However, it may be possible to tap into this recalcitrant P pool thereby drastically expanding the volumes of struvite that could be derived from pig farms. In this area, **we recommend firstly screening the proportions of available P from the diverse range of Australia's piggery effluent management systems.** Following on from this, **rigorous testing of approaches to mobilise P from the effluent stream is suggested,** including methods such as physical treatment (e.g., mixing, sonication, shock wave), chemical manipulation (e.g., fermentation, acid dosing) and biological techniques (microbial and enzyme dosing). Testing novel approaches to deliver other key components for struvite precipitation is also encouraged. For example, screening Mg-rich bore water supplies in close proximity to piggery enterprises might offer a way forward to viably deliver this often-limiting element to struvite precipitation. To establish an optimal pH for struvite precipitation, research into manure and urea hydrolysis rates and their interplay with competing fermentation and volatilisation processes in effluent systems is recommended.

With regards to agronomic performance, long-term field experiments testing struvite effectiveness in alkaline soils are lacking. Much of Australia's productive cropping land is situated on alkaline clayey vertosols. **We therefore recommend struvite testing in these types of settings.** These field trials need to focus not only on the immediate responses of plant growth under struvite treatments, but also on multiple-season long-term outcomes given that struvite-soil rhizosphere interactions are potentially complex and may take some time to reach steady state. **Investigations into the role of organic 'impurities' in piggery struvite on agronomic performance will also be extremely valuable given that this component of the struvite might well convey plant growth promoting benefits as well as improved long-term soil function.** In tandem with this focus on alkaline soils, **parallel assessments of struvite effects on soils impacted by acidification** would be very useful for gaining knowledge on the potential for struvite to remediate these types of landscapes, as well as offering nutrient supply. In balance with this agronomic aspect, **further work is needed to anticipate governance and regulatory requirements associated with the application of piggery-derived struvite fertilizers.** This aspect alone could be the single most important factor in determining the viability of struvite use in agricultural landscapes.

Finally, **a dedicated economic and adoption analysis of the complete process of struvite extraction and application is needed.** In this review we have provided information on struvite economic value from limited reports and case studies based largely overseas. We found a wide range in estimates of struvite prices reportedly needed to achieve viable economic returns. On the basis of these varying reports, **we recommend a targeted economic analysis of the extraction and production process based on Australian-focused inputs.** Subject to positive conclusions arising from this financial analysis, **we recommend that a qualified social scientist work closely with producers and end-users in order to address the opportunities and obstacles associated with widespread roll-out of the technology.**

7. Conclusions

- Struvite recovery from piggery effluent is clearly technically feasible, as evidenced by successful pilot-scale demonstrations conducted in Australia and overseas.
- Based on current effluent management practices, the proportion of phosphorus (P) in piggery effluent that is available for recovery by struvite precipitation is quite low (approximately 15%). This proportion could be increased through approaches aimed at releasing P from the largely insoluble fraction associated with particulate matter that ends up in sludge.
- Other parameters crucial for struvite precipitation, notably magnesium and nitrogen supply and pH adjustment could be further optimised for piggery effluent.
- Long-term agronomic trials testing piggery-derived struvite efficiency in alkaline soils, which are common in the Australian agricultural landscape, are critically needed.
- It will be valuable to assess potential production advantages in combination with any observed benefit to soil health and function elicited by piggery-derived struvite relative to conventional fertilizers.
- Many Australian agricultural soils are experiencing acidification problems, and it will be useful to test the effect of struvite in these locations given struvite has the potential to deliver twinned benefits of acid mitigation and nutrient delivery.
- Government regulation requirements associated with applying piggery-derived struvite as a fertilizer are not well-understood and efforts are encouraged to anticipate how the legislative framework would apply.
- Based on current factors it appears that the economics of struvite recovery and fertilizer development from Australia's piggery effluent are marginal. However, specific reports on the economics of full-scale application of struvite as a fertilizer material, sourced solely from overseas, are highly variable. As a result, a dedicated economic analysis as well as an adoption appraisal is recommended in order to evaluate the opportunities and obstacles associated with widespread roll-out of the technology in relation to the Australian pork industry.

8. Literature Cited

Achat, D.L., Sperandio, M., Daumer, M.-L., Santellani, A.-C., Prud'Homme, L., Akhtar, M., Morel, C., 2014. Plant-availability of phosphorus recycled from pig manures and dairy effluents as assessed by isotopic labeling techniques. *Geoderma* 232–234, 24-33.

Adnan, A., Koch, F.A., Mavinic, D.S., 2003. Pilot-scale study of phosphorus recovery through struvite crystallization – II: Applying in-reactor supersaturation ratio as a process control parameter. *Journal of Environmental Engineering and Science* 2, 473-483.

Ahmed, S., Y. , Shiel, R., S. , Manning, D.A.C., 2006. Use of struvite, a novel P source derived from wastewater treatment, in wheat cultivation. In: 18th World Congress of Soil Science, Soil Science Society of America, Philadelphia, Pennsylvania, USA, pp. 9-15.

Baker, D., 2000. *Swine Nutrition*. CRC Press, Boca Raton

Bridger, G.L., Salutsky, M.L., Starostka, R.W., 1962. Micronutrient sources, metal ammonium phosphates as fertilizers. *Journal of Agricultural and Food Chemistry* 10, 181-188.

Burgess, J., Batstone, D.J., Muster, T., F., P., 2015. *Wastewater—an Untapped Resource?* Australian Academy of Technological Sciences and Engineering.

Burns, R., T., Moody, L., B., Walker, F., R. , Raman, D., R., 2001. Laboratory and in-situ reductions of soluble phosphorus in swine waste slurries. *Environmental Technology* 22, 1273-1278.

Burns, R.T., Moody, L.B., Celen, I., Buchanan, J.R., 2003. Optimization of phosphorus precipitation from swine manure slurries to enhance recovery. *Water Science and Technology* 48, 139-146.

Cabeza, R., Steingrobe, B., Römer, W., Claassen, N., 2011. Effectiveness of recycled P products as P fertilizers, as evaluated in pot experiments. *Nutrient Cycling in Agroecosystems* 91, 173-184.

Canh, T.T., Aarnink, A.J.A., Schutte, J.B., Sutton, A.L., Langhout, D.J., Verstegen, M.W.A., 1998. Dietary protein affects nitrogen excretion and ammonia emission from slurry of growing-finishing pigs. *Livestock Production Science* 56, 181-191.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications* 8, 559-568.

Çelen, I., Buchanan, J.R., Burns, R.T., Bruce Robinson, R., Raj Raman, D., 2007. Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. *Water Research* 41, 1689-1696.

Collavino, M.M., Sansberro, P.A., Mroginski, L.A., Aguilar, O.M., 2010. Comparison of in vitro solubilization activity of diverse phosphate-solubilizing bacteria native to acid soil and their ability to promote *Phaseolus vulgaris* growth. *Biology and Fertility of Soils* 46, 727-738.

Cordell, D., Drangert, J.-O., White, S., 2009. The story of phosphorus: Global food security and food for thought. *Global Environmental Change* 19, 292-305.

Cordell, D., Neset, T.S.S., 2014. Phosphorus vulnerability: A qualitative framework for assessing the vulnerability of national and regional food systems to the multi-dimensional stressors of phosphorus scarcity. *Global Environmental Change* 24, 108-122.

Dai, X., Karring, H., 2014. A determination and comparison of urease activity in feces and fresh manure from pig and cattle in relation to ammonia production and pH changes. *PLoS ONE* 9, e110402.

- Doyle, J.D., Oldring, K., Churchley, J., Parsons, S.A., 2002. Struvite formation and the fouling propensity of different materials. *Water Research* 36, 3971-3978.
- Elser, J.J., Elser, T.J., Carpenter, S.R., Brock, W.A., 2014. Regime shift in fertilizer commodities indicates more turbulence ahead for food security. *PLoS ONE* 9, e93998.
- FAO, 2016. World fertilizer trends and outlook to 2019. Summary Report. Food and Agriculture Organization of the United Nations, Rome.
- Gaterell, M.R., Gay, R., Wilson, R., Gochin, R.J., Lester, J.N., 2000. An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets. *Environmental Technology* 21, 1067-1084.
- Ghosh, G.K., Mohan, K.S., Sarkar, A.K., 1996. Characterization of soil-fertilizer P reaction products and their evaluation as sources of P for gram (*Cicer arietinum* L.). *Nutrient Cycling in Agroecosystems* 46, 71-79.
- González-Ponce, R., López-de-Sá, E.G., Plaza, C., 2009. Lettuce response to phosphorus fertilization with struvite recovered from municipal wastewater. *HortScience* 44, 426-430.
- Heffer, P., 2009. Assessment of fertilizer use by crop at the global level. In: International Fertilizer Industry Association (IFA) (Ed.), *AgCom/09/28 Paris*.
- Huang, H., Liu, J., Ding, L., 2015. Recovery of phosphate and ammonia nitrogen from the anaerobic digestion supernatant of activated sludge by chemical precipitation. *Journal of Cleaner Production* 102, 437-446.
- Huang, H., Liu, J., Wang, S., Jiang, Y., Xiao, D., Ding, L., Gao, F., 2016a. Nutrients removal from swine wastewater by struvite precipitation recycling technology with the use of $Mg_3(PO_4)_2$ as active component. *Ecological Engineering* 92, 111-118.
- Huang, H., Zhang, P., Zhang, Z., Liu, J., Xiao, J., Gao, F., 2016b. Simultaneous removal of ammonia nitrogen and recovery of phosphate from swine wastewater by struvite electrochemical precipitation and recycling technology. *Journal of Cleaner Production* 127, 302-310.
- Humer, E., Schwarz, C., Schedle, K., 2015. Phytate in pig and poultry nutrition. *Journal of Animal Physiology and Animal Nutrition* 99, 605-625.
- Ichihashi, O., Hirooka, K., 2012. Removal and recovery of phosphorus as struvite from swine wastewater using microbial fuel cell. *Bioresource Technology* 114, 303-307.
- Jia, G., Zhang, H., Krampe, J., Muster, T., Gao, B., Zhu, N., Jin, B., 2017. Applying a chemical equilibrium model for optimizing struvite precipitation for ammonium recovery from anaerobic digester effluent. *Journal of Cleaner Production* 147, 297-305.
- Johnson, S.E., Loeppert, R.H., 2006. Role of organic acids in phosphate mobilization from iron oxide. *Soil Science Society of America Journal* 70, 222-234.
- Johnston, A.E., Richards, I.R., 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use and Management* 19, 45-49.
- Jones, D.L., Dennis, P.G., Owen, A.G., van Hees, P.A.W., 2003. Organic acid behavior in soils – misconceptions and knowledge gaps. *Plant and Soil* 248, 31-41.

KochFertiliserTM, 2017. Koch Fertiliser Australia Pty Ltd. <http://kochfertaustralia.com/>. Accessed 30th June 2017.

Kumar, R., Pal, P., 2015. Assessing the feasibility of N and P recovery by struvite precipitation from nutrient-rich wastewater: a review. *Environmental Science and Pollution Research* 22, 17453-17464.

Laridi, R., Auclair, J.C., Benmoussa, H., 2005. Laboratory and pilot-scale phosphate and ammonium removal by controlled struvite precipitation following coagulation and flocculation of swine wastewater. *Environmental Technology* 26, 525-536.

Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A., 2005. Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth* 283, 514-522.

Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A., 2009. Phosphorus recovery from wastewater by struvite crystallization: A review. *Critical Reviews in Environmental Science and Technology* 39, 433-477.

Li, X.Z., Zhao, Q.L., 2003. Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer. *Ecological Engineering* 20, 171-181.

Liu, Y., Kumar, S., Kwag, J., Kim, J., Kim, J., Ra, C., 2011a. Recycle of electrolytically dissolved struvite as an alternative to enhance phosphate and nitrogen recovery from swine wastewater. *Journal of Hazardous Materials* 195, 175-181.

Liu, Y., Kwag, J.-H., Kim, J.-H., Ra, C., 2011b. Recovery of nitrogen and phosphorus by struvite crystallization from swine wastewater. *Desalination* 277, 364-369.

Malusá, E., Sas-Paszt, L., Ciesielska, J., 2012. Technologies for beneficial microorganisms inocula used as biofertilizers. *The Scientific World Journal* 2012, 12.

Manas, A., Sperandio, M., Decker, F., Biscans, B., 2012. Location and chemical composition of microbially induced phosphorus precipitates in anaerobic and aerobic granular sludge. *Environmental Technology* 33, 2195-2209.

Mander, C., Wakelin, S., Young, S., Condron, L., O'Callaghan, M., 2012. Incidence and diversity of phosphate-solubilising bacteria are linked to phosphorus status in grassland soils. *Soil Biology and Biochemistry* 44, 93-101.

Massey, M.S., Davis, J.G., Ippolito, J.A., Sheffield, R.E., 2009. Effectiveness of recovered magnesium phosphates as fertilizers in neutral and slightly alkaline soils. *Agronomy Journal* 101, 323-329.

Matynia, A., Wierzbowska, B., Hutnik, N., Mazienczuk, A., Kozik, A., Piotrowski, K., 2013. Separation of struvite from mineral fertilizer industry wastewater. *Procedia Environmental Sciences* 18, 766-775.

Mehta, C., 2015. Fertilisers from piggery liquid effluent via nutrient extraction. *Advanced Water Management Centre University of Queensland Report Prepared for the Department of Agriculture and Fisheries, Queensland*.

Mehta, C., 2016. Fertilisers from piggery liquid effluent via nutrient extraction. *The University of Queensland - report prepared for the Department of Agriculture and Fisheries*, pp. 1-19.

Molinos-Senante, M., Hernández-Sancho, F., Sala-Garrido, R., Garrido-Baserba, M., 2011. Economic feasibility study for phosphorus recovery processes. *Ambio* 40, 408-416.

Münch, E.V., Barr, K., 2001. Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams. *Water Research* 35, 151-159.

Murray, J., 1858. Notices and Abstracts. British Association for the Advancement of Science, pp 54–55.

NLWRA, 2001. Australian dryland salinity assessment 2000: extent, impacts, processes, monitoring and management options. National Land and Water Resources Audit c/o Land & Water Australia On behalf of the Commonwealth of Australia

Poad, G., McGahan, E., 2010. Exploration of the opportunities to establish anaerobic digestion for the generation of biogas. Final Report. In: Consulting, F. (Ed.), APL Project 2009/2293, Toowoomba Qld 4350.

Rahman, M.M., Liu, Y., Kwag, J.-H., Ra, C., 2011. Recovery of struvite from animal wastewater and its nutrient leaching loss in soil. *Journal of Hazardous Materials* 186, 2026-2030.

Rahman, M.M., Salleh, M.A.M., Rashid, U., Ahsan, A., Hossain, M.M., Ra, C.S., 2014. Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review. *Arabian Journal of Chemistry* 7, 139-155.

Regy, S., Mangin, D., Klein, J.P., Lieto, J., 2002. Phosphate recovery by struvite precipitation in a stirred reactor. Report, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), Centre Européen d'Etude des Polyphosphates, Brussels, Belgium. <http://www.phosphorusplatform.eu/images/download/Regy-Mangin-Lagep-Report-struvite-precipitation-2001.pdf>

Ren, L., Schuchardt, F., Shen, Y., Li, G., Li, C., 2010. Impact of struvite crystallization on nitrogen losses during composting of pig manure and cornstalk. *Waste Management* 30, 885-892.

Ryu, H.-D., Lee, S.-I., 2016. Struvite recovery from swine wastewater and its assessment as a fertilizer. *Environmental Engineering Research* 21, 29-35.

Ryu, H.-D., Lim, C.-S., Kang, M.-K., Lee, S.-I., 2012. Evaluation of struvite obtained from semiconductor wastewater as a fertilizer in cultivating Chinese cabbage. *Journal of Hazardous Materials* 221–222, 248-255.

Smith, V.H., Tilman, G.D., Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution* 100, 179-196.

Song, Y.-H., Qiu, G.-L., Yuan, P., Cui, X.-Y., Peng, J.-F., Zeng, P., Duan, L., Xiang, L.-C., Qian, F., 2011. Nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization without chemical additions. *Journal of Hazardous Materials* 190, 140-149.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y., 2005. Recovery of phosphorous from swine wastewater through crystallization. *Bioresource Technology* 96, 1544-1550.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y., Yasuda, T., Waki, M., 2007. Removal and recovery of phosphorous from swine wastewater by demonstration crystallization reactor and struvite accumulation device. *Bioresource Technology* 98, 1573-1578.

Svoboda, I., 2003. Anaerobic digestion, storage, oligolysis, lime, heat and aerobic treatment of livestock manures, Final Report, Provision of research and design of pilot schemes to minimise livestock pollution to the water environment in Scotland. FEC Services Ltd., Kenilworth, Warwickshire.

Talboys, P.J., Heppell, J., Roose, T., Healey, J.R., Jones, D.L., Withers, P.J.A., 2016. Struvite: a slow-release fertiliser for sustainable phosphorus management? *Plant and Soil* 401, 109-123.

Tao, W., Fattah, K.P., Huchzermeier, M.P., 2016. Struvite recovery from anaerobically digested dairy manure: A review of application potential and hindrances. *Journal of Environmental Management* 169, 46-57.

Tucker, R., 2015. Piggery manure and effluent management and reuse guidelines. Australian Pork Limited.

Weast, R., 1970. *CRC handbook of chemistry and physics*. CRC Press, Cleveland.

Yetilmezsoy, K., Ilhan, F., Kocak, E., Akbin, H.M., 2017. Feasibility of struvite recovery process for fertilizer industry: A study of financial and economic analysis. *Journal of Cleaner Production* 152, 88-102.

Yetilmezsoy, K., Sapci-Zengin, Z., 2009. Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer. *Journal of Hazardous Materials* 166, 260-269.

Zhang, D.-m., Chen, Y.-x., Jilani, G., Wu, W.-x., Liu, W.-l., Han, Z.-y., 2012. Optimization of struvite crystallization protocol for pretreating the swine wastewater and its impact on subsequent anaerobic biodegradation of pollutants. *Bioresource Technology* 116, 386-395.

Zhang, T., Ding, L., Ren, H., 2009. Pretreatment of ammonium removal from landfill leachate by chemical precipitation. *Journal of Hazardous Materials* 166, 911-915.