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Phosphorus speciation and fertiliser performance characteristics: a comparison of waste recovered struvites from global sources

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Graphic Abstract

Abstract

Our immediate and future food security agenda requires sustainable phosphorus (P) management, and recovered P products such as struvite form part of the solution. Waste recovered struvite is generated from different waste streams and precipitation technologies. In this study, we compare P speciation and bioavailability of nine struvite products with traditional/granulated chemical fertilisers to investigate performance characteristics across soil types in the Irish ecoregion. Elemental-analysis/P-speciation of the struvites was examined by ICP-OES, ³¹P solid state NMR, PXRD and P-solubility tests. The fertiliser dose effect and bioavailability of the different struvite products were tested in 4-week and 3-month rhizotron experiments with *Lolium perenne*. In addition to calculating plant-P offtake, bioavailability was assessed by Olsen-P and Diffusive-Gradients-in-Thin-Films (DGT). The struvites differed markedly in colour/appearance, texture, metal content and solubility. Struvites all had similar P-speciation, but minor impurity phases were detected. There was no significant difference between the struvite samples and triple-superphosphate (TSP) with respect to either plant growth performance or P-bioavailability. The struvite

products are produced from different wastewater streams/processes, yet possess a uniformity in overall fertilising performance within our experiments. Encouragingly, no appreciable agronomic difference in terms of yield was observed between the struvite and chemical fertilisers, which provides further evidence in support of struvite as a sustainable alternative to mined rock-phosphate derived products. Importantly the struvite samples analysed within this study contained both significantly fewer impurities than TSP and lower concentrations of toxic metals such as cadmium.

Keywords: Phosphorus, Struvite, X-ray diffraction analysis, Chemical analysis, Spectroscopy, inductively coupled plasma methods.

Abbreviations

DGT diffusive gradients in thin films

P_{DGT} Phosphorus concentration from DGT

ICP-OES inductively coupled plasma optical emission spectroscopy

MAP mono-ammonium phosphate

MAS magic angle spinning

SSNMR solid state nuclear magnetic resonance

P phosphorus

ppm parts per million

PXRD powder X-ray diffraction

TSP triple superphosphate

MAP mono-ammonium phosphate

XIA Xiamen

- 69 CGS Crystal Green 1.5mm
- 70 CGL Crystal Green 3mm
- 71 AAS Aaby small
- 72 AAM Aaby medium
- 73 AAL Aaby large
- 74 HER Herning
- 75 HEL Helsingør
- 76 BER BerlinerPflanzeTM
- 77
- 78

1.0 Introduction

Phosphorus (P) is a limited and life-essential element (Cordell and White 2011). P capture as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) at wastewater treatment plants provides a sustainable recovery method and aims to protect water quality (Desmidt et al. 2015, Mayer et al. 2016). Waste recovered struvite production has been optimised via a handful of patented precipitation technologies developed principally for application in municipal wastewater (Desmidt et al. 2015). Although struvite precipitation from dairy, urine, swine manure, and semiconductor wastes is now also practised (Li et al. 2019), struvite is considered to be a slow-release P fertiliser, which means that it has a delayed dissolution in soil. This kinetic characteristic has agronomic advantages, principally because P can be released to the soil porewater throughout the growing season (Talboys et al. 2016). Waste recovered struvite has thus been shown to be an effective soil additive for several crops, with similar yields being reported when compared with traditional inorganic P fertiliser [triple-super-phosphate (TSP)] (Ahmed et al. 2018, Li et al. 2019). Although published data on the performance of waste recovered P fertilisers is increasing (Johnston and Richards 2003; Ali et al., 2005), the different chemical behaviours of struvite, particularly across differing soil types is less well understood (Symanska et al., 2019).

Several factors impact on the bioavailability of struvite. The positive effect of struvite on above-ground biomass has been well-established for low-pH soils with high proton/ H^+ concentrations (Hilt et al. 2016; Degryse et al. 2017), with the pH minimum of solubility for struvites being ~9.0-11 (Ali et al. 2004). Nevertheless, struvites have also been found to be an efficient fertiliser at neutral and alkaline soil pH (Massey et al. 2009, Uysal and Kuru 2015). This seems counter-intuitive, but Talboys et al. (2016) demonstrated that the fertiliser effect was activated by localised excretion of organic acids from plant roots (Jones 1998), highlighting the importance of the plant-soil interface when understanding struvite performance. A further consideration is that as soil P adsorption capacity increases for example in iron (Fe) and aluminium (Al) rich soils, this could

promote further struvite solubilisation because adsorption of P onto soil particles lowers the concentration in soil porewater and drives struvite dissolution (Degryse et al. 2017). P solubilisation from struvite is also influenced by the particle size, with smaller grain sizes exhibiting faster reaction rates (Degryse et al. 2017). One of the main advantages of struvite relates therefore to the potential benefit for water quality in terms of reducing P loss from land to water, when compared to fertilisation with highly soluble fertilisers such as TSP and monoammonium phosphate (MAP) (Talboys et al. 2016, Withers et al. 2014b) (Talboys et al. 2016; Withers et al. 2014).

Despite the potential of waste recovered struvites, their reported chemical compositions are not always consistent with pure struvite, which is 12.6 % P, 9.9 % magnesium (Mg), and 5.7 % nitrogen (N) (w/w %) (Ahmed et al. 2018). Furthermore, metal impurities such as Al, Fe, calcium (Ca), and small amounts of heavy metals can also precipitate along with the struvite (Li et al. 2019). Such inconsistency in composition was observed by Cabeza et al. (2011) for three struvite products from three separate wastewater treatment plants. In this study struvite from the Gifhorn wastewater treatment plant, Germany (WWTP) contained large amounts of Ca (8.6) and Fe (5.5), and only 5.5 % Mg, whereas the other two products contained 8.5-8.8 % Mg resulting in a much lower water solubility (Cabeza et al. 2011). It is unknown if this variation in water solubility was due simply to the presence of metal impurities, or if the metal impurities had immobilized some of the phosphate in inorganic forms other than struvite. It has been demonstrated that struvite synthesized with excess Mg directly decreases the solubilisation of struvite in soil (Degryse et al. 2017). Johnston and Richards (2003) investigated the difference in P bioavailability from recovered P products and found no statistical difference between the biomass yield of perennial ryegrass grown with struvite precipitated from different waste streams, including municipal sewage, corn steep liquor, veal manure, and industrial wastewater (Johnston and Richards 2003).

However, the P speciation of these struvite products was not determined, which potentially complicates the interpretation of bioavailability.

Most studies to date have tended to focus on struvite from a single precipitation facility, therefore cross-sectoral differences between struvite products, stemming from variations in wastewater composition and/or the technological process applied, has largely not been investigated. Even within municipal WWTPs, there can be a significant difference in the size of the facilities, wastewater composition (domestic or industrial), treatment processes and the type of struvite precipitation technology used. As a result there are multiple factors that could potentially lead to inconsistency in the composition, speciation and behaviour of waste recovered P (Lu et al. 2016, Ma et al. 2014).

Even though crop response to fertilisation with struvite recovered from wastewater has been investigated (Ahmed et al. 2018), to the best of our knowledge it has not been considered alongside detailed P speciation analysis of struvite. Struvite has nevertheless been characterized by ^{31}P solid state nuclear magnetic resonance (SSNMR) in kidney stones (Bak et al. 2000), dental materials (Scrimgeour et al. 2007), poultry litter (Hunger et al. 2008), and laboratory synthesized struvite (Ma et al. 2014, Sugiyama et al. 2005). Powder X-ray diffraction (PXRD) of some struvite products has shown the presence of newberyite $\text{Mg}(\text{HPO}_4)\cdot 3\text{H}_2\text{O}$ (Lu et al. 2016, Zhang et al. 2016). Powder X-ray diffraction, however, only identifies crystalline phases and ignores potential crystal-to-amorphous transformations. The lack of a complete understanding of P speciation patterns in struvite potentially complicates/impairs our interpretation of P availability *in solum*, since without full P speciation characterisation it is impossible to decipher, authoritatively, the mechanisms of P release.

P bioavailability and plant uptake is a complex disequilibrium, as the balance between varying P sorption mechanisms continually changes, with no single technology or methodology mimicking

exactly the *in situ* elemental flows. Agronomic and environmental tests for soil bioavailable P are often based on measurements of sodium bicarbonate extractable-P (Olsen-P), but this methodology has been shown to underestimate bioavailable P in acidic or Fe and Al rich soils (Bell et al., 2005) and operates far outside the norms of pH (8.5) usually encountered within most soils. An alternative advanced speciation method, namely DGT (Diffusive Gradients in Thin films), which is a passive sampling technology has been compared with Olsen-P (Mason et al., 2010) in field trials and yields an enhanced representation of the plant available P pool and supply flux for labile solutes. Using a DGT passive sampler allows access to the surface binding sites in a controlled and less chemically invasive manner compared to standard extraction methods, similar to the diffusive action of a plant root. However, when these operationally distinct soil tests are used in tandem, identifying differences between the measurements provides further clarity as to how the collective mechanisms of P release are operating for a given soil, fertiliser or plant interaction.

In this study we investigate the composition, speciation and bioavailability of a range of struvite products, sourced from around the world, made by full-scale struvite precipitation from wastewater by the main technologies in operation to date.

Here we specifically investigate the following:

1. Does elemental composition, P speciation and solubility vary across the nine struvite products analysed within this study? How do these struvite products compare with the traditional agronomically applied chemical fertilisers?
2. Do differences exist between the struvite products using plant experiments (short term – 4-week; long term – 3-month) with *L. perenne*? Specifically does a) fertiliser performance characteristics vary across the struvite products on low index-P Irish soils; b) what is the

influence of soil pH and c) how does struvite performance compare with traditional granular/chemical P fertilisers?

2.0 Material and Methods

2.1 Characteristics of recovered fertilisers

The struvite products used in this study are described in Fig. 1 and the location and technology used for their production are shown in Table 1 (further details are provided in the Supporting Information, SI). Waste recovered struvite samples were selected to represent a range of available struvites from diverse geographic origins. The struvite products are referred to using the following abbreviations: Herning (HER; Denmark), Aaby small (AAS; Denmark), Aaby medium (AAM; Denmark), Aaby large (AAM; Denmark), Helsingør (HEL; Denmark), Xiamen (XIA; China), BerlinerPflanzeTM (BER; Germany), Crystal green 1.5 mm (CGS; Netherlands), and Crystal green 3 mm (CGL; Netherlands) and mono-ammonium phosphate. All fertiliser samples were ground using a Retsch PM100 ball mill and sieved to <2mm before analysis.

2.2 Elemental and Speciation analysis

To investigate the metal composition and P content of the struvite products elemental analysis was performed using ICP-OES (Perkin Elmer Optima 2100 DV). Further details on the instrument set-up are provided in the SI.

2.2.1 ³¹P magic angle spinning solid state NMR spectroscopy. Solid state ³¹P NMR spectroscopy was performed at 11.7 T on a 500 MHz Jeol ECZ 500R spectrometer with a 3.2 mm Jeol MAS

NMR probe. Quantitative ^{31}P MAS NMR spectra (45° flip angle) were recorded for all fertiliser samples with 15 kHz magic angle spinning (MAS). The carrier frequency was set at -9 ppm. The recycle delay was optimized for each sample and set to $5 \cdot T_1$ for the P signal in the sample with longest relaxation, as determined from inversion recovery experiments. Typical recycle delays chosen were 130-800 seconds. Spectra were referenced to H_3PO_4 ($\delta(^{31}\text{P}) = 0$ ppm), and single-pulse ^{31}P SSNMR spectra were analysed by absolute integration of the resonances in MestReNova after baseline correction using a pure sample of struvite as an external reference (Staal et al. 2019). When spinning side bands were present, they were included in the integration of the signals.

2.2.2 Powder X-Ray diffraction. PXRD diffractograms were recorded on a Rigaku Miniflex 600 diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The data were recorded in the range $2\theta = 3$ - 90° with a step size of 0.02 and a speed $10^\circ/\text{min}$. The software PDXL2 from Rigaku was used to match diffractograms with the ICDD library.

2.2.3 Solubility extractions

Tests using H_2O and 1M HCl extractions were carried out to test the solubility differences of the struvite in neutral and acidic solutions. Extractants were made up using water with a resistance of 18.2 M Ω .cm (at 25°C) which were randomly tested using the Molybdenum blue method (Murphy and Riley 1962) to check for a low P concentration ($<\text{LOD}$). All fertiliser samples were extracted at a ratio of 1:125 (struvite: extractant solution) in their corresponding H_2O and 1M HCl solutions and shaken for 30 minutes at a stable temperature. All samples were centrifuged and filtered, and P content analysed colorimetrically using the Molybdate-blue method (Murphy and Riley 1962). Unplanted soil incubation experiments were used as controls throughout, conducted alongside Experiment A and B (*soil treatment and experimental design described below*) and measured by DGT analysis.

223

224 2.3 Plant Experiments

225 2.3.1 *Soil characteristics*. The three soils used in this experiment were all collected in Northern
226 Ireland (NI) and ordered via the NI soil classification system (Table 2). The soils were specifically
227 selected to: a) represent the dominant soil types of NI, these being Brown Earth and Gley, b) have
228 a P index of 0, and c) exhibit a natural variation in Irish soil pH. The soil used in the 4-week
229 experiment is a Brown Earth (soil 1) collected in Hillsborough, NI (Grid reference: NW355126)
230 from unfertilised field boundaries situated between intensively managed/long-term grassland
231 pasture. The first soil used in the long-term (3 month) plant pot experiment was also a Brown Earth
232 (soil 2) collected from the Agri-Food and Biosciences Institute (AFBI), Crossnacreevy
233 experimental farm (Grid reference: NW512241). The second soil used in the long-term pot
234 experiment was a Mineral Gley soil 3) collected at Garvagh, NI (Grid reference: NW022776). Soil
235 3 was collected from the field boundary on unfertilised soil from a long-term grass rotation.

236

237 2.3.2 *Experiment A*. The fertiliser performance of the struvite products was tested in a short-term
238 (4-week) experiment under highly controlled environmental/growth chamber conditions with
239 perennial ryegrass, to investigate fertiliser performance across the soil types over a range of
240 amendment doses (25, 50 and 100 kg P ha⁻¹). Early stage rhizosphere formation was induced in
241 homogeneously packed soil columns (250g soil; 10 x 6.8cm) by transplanting a standardised
242 biomass of seedlings (~25 plants, 4 replicates of each treatment) to create a uniform environment
243 to isolate plant-soil-fertiliser interactions.

244

245 The recommended P fertiliser level for grass establishment on NI soils with P-index 0 (Olsen-P 0-
246 9 mg P kg⁻¹ soil) is 120 kg P₂O₅ ha⁻¹, corresponding to 52.3 kg P ha⁻¹ (AHDB 2018). Struvite
247 products and chemical fertilisers were ground and added at three levels: the RB209 recommended

level (50 kg P ha⁻¹, corresponding to 73 mg P kg dry soil⁻¹), a low level (25 kg P ha⁻¹, corresponding to 36 mg P kg dry soil⁻¹) and a high level (100 kg P ha⁻¹, corresponding to 146 mg P kg dry soil⁻¹). Ground TSP was added at five levels and served as a control response curve with the following doses: 0, 12.5, 25, 50, and 100 kg P ha⁻¹. The fertilisers were dosed based on their total P content to ensure that all pots received the same amount of total P. Each soil batch was prepared in the same way: 250 g of dry soil (sieved to <2mm) was mixed with a corresponding addition of P fertiliser, along with a replete supply of N in the form of 125 mg urea. Nitrogen dosing was undertaken to standardise the experimental conditions and to isolate the impact of P uptake by the plant. Further information on the experimental set-up is provided in the SI.

2.3.3 Experiment B. A 3-month greenhouse/mesocosm trial (5 kg soil; 30 x 25cm, n=3) where the different struvites were interrogated using two soils of differing pH (soil 2: pH 6.2 and soil 3: pH 5.4), to consider plant growth and plant-soil-fertiliser interactions over a longer time interval.

Soils were treated with a fertiliser dose of 50 kg P ha⁻¹ and equivalent N (Urea). Soil 2 was treated with the same fertilisers as the 4-week perennial ryegrass experiment (No P addition, TSP, MAP, XIA, CGL, AAS, HER, BER) whilst soil 3 was only treated with commercially available fertilisers TSP, XIA, CGL, BER and a control treatment with no P addition. Fertilisers were applied to the top layer of soil and mixed by hand to get a homogenous distribution. Soils were left to equilibrate for 4 days and maintained at 65% WHC. The same Perennial ryegrass germination procedures as for the 4-week trial (Exp. A) were followed with 20g of wet biomass transferred into the prepared soil mesocosms (sieved <2mm). The growth period spanned 3 months with assisted heat and lighting supplied from 8am-8pm. Perennial ryegrass shoots and soils were harvested and treated with same protocol from experiment A.

2.4 Plant and soil analyses

Close-coupled cartesian geometry configured energy dispersive X-Ray Fluorescence (XRF) spectrometry (Rigaku NEX CG) with a fundamental parameters (FP) calibration was used for elemental profiling of soils and ryegrass samples which yielded ≥ 3 g DM. For quality control, certified reference material (CRM) of Polish mixed herbs (INCT-MPH-2) and soil (ISE 921) were used. The average elemental recovery was 102 +/- 15% for plant and 110 +/- 8% for soil, a full summary is provided in the SI.

Where < 3 g DM yield was obtained concentrations of P, Mg, Ca, K and S were measured after microwave digestion of 0.25 g of plant material in 5 mL of concentrated nitric acid (CEM Corporation 2004, Havlin and Soltanpour 1980, Zarcinas et al. 1987). The elements were measured by ICP-OES on an Agilent 5100 at the Agri -Food Bioscience Institute (AFBI), Newforge Lane, Northern Ireland. Total N was measured by dry combustion on a TruMac N (LECO Corporation 2012). Total P in plant shoots were multiplied by DM yield to obtain shoot P offtake per treatment in all plant samples.

2.4.2 Olsen-P measurements of plant available P. Methods for Olsen P extraction were as reported by Bell et al. (2005). Soil samples were dried (30°C) and sieved to < 2 mm. Olsen P was extracted using 5% bicarbonate buffered at pH 8.5, in a soil solution ratio 1:20 v/v (Bell et al. 2005, Olsen et al. 1954). The extraction time was 30 minutes at a controlled temperature (22°C) and samples were then centrifuged to remove the supernatant. The molybdate blue method of Murphy and Riley (1962) was used to determine available P in the sample with modified volumes of 230 μ l of sample and 20 μ l of molybdenum blue reagent. A 96 well microplate reader with ultra-clear polystyrene microplates was used for analysis, with three analytical replicates per soil sample.

2.4.3 DGT measurements of plant available P. DGT methods were carried out according to Davison and Zhang (1994) as described by Mason et al. (2008) (see SI, section S11). Binding and diffusive gels were supplied by DGT Research Ltd. Flat sheets (approx. 130 x 130 mm) of standard (APA), 0.8 mm thick diffusive gel, and 0.4 mm thick FeOH binding gels were cut using the same non-metallic cylindrical cutter (25 mm diameter) for accuracy and consistency. All DGT devices were deployed in 20 g of dry soil wetted to WHC for 24 hrs in a 35 mm diameter petri dish. The binding gels were extracted from the DGT devices upon retrieval and eluted in 1 mL of 1 M HCL solution and measured colorimetrically using the Molybdate-blue method (Murphy and Riley 1962) to determine P_{DGT} .

2.5 Statistical analysis

Data processing and statistical analyses was performed in minitab v. 18 and Prism 8. General Linear Model (GLM) with interaction and Tukey Pairwise comparisons and Principal Component Analysis (PCA) were conducted using Minitab 18 and Regression analysis was conducted using Prism 8. An overview of the performed GLMs can be found in the SI (Table S5).

3.0 Results

3.1 Elemental composition using ICP-OES, ^{31}P SSNMR spectroscopy and PXRD.

The P concentration of the struvite products varied from 9.0 to 13.6 % P and the Mg concentrations were in the range 7.7 to 11.0 % Mg (Fig. 2 and Table S1). Thus, the P and Mg contents of some of the struvite products deviated somewhat from the theoretical P and Mg composition of pure struvite, which are 12.6 % and 9.9 %, respectively. The BER and HEL samples contain less P than expected, i.e. 9.0 % P for the BER sample and 10.9 % P for the HEL sample. The other struvite products had P contents either close to the theoretical composition or else contained excess P (Fig.

2 and Table S2). All struvite products contained less P than the TSP, which had 21% P. Most of the struvite products contained excess Mg (between 1 and 11%) compared to the theoretical composition, with the exception of samples BER (7.7 %) and HEL (9.5 %).

Differences in metal impurities existed between the struvite products (Fig. 2 and Table S3). The BER sample contained a variety of notable metal impurities/enrichments (Al, Fe, Ca, Cu, Zn, Pb, and Mn). The amount of metal impurities varied greatly among the remaining struvite products, e.g. Fe concentration in BER (2993 mg kg⁻¹) and HER (1349 mg kg⁻¹) which were substantially higher than the other struvite products (which typically contained 10-290 mg kg⁻¹ Fe). The BER, and HER samples also contained more Al than the other struvite products, 432 mg kg⁻¹ and 33 mg kg⁻¹, respectively. Ca content also differs among the struvite products, with BER, HER and XIA having the highest Ca values at 6,823 mg kg⁻¹, 1,063 mg kg⁻¹, and 1,096 mg kg⁻¹, respectively. The BER sample also contained a relatively high concentration of Zn, over five-fold more than any of the other struvites, but this was accompanied by an enrichment in Pb of 14 mg kg⁻¹ (Table S3). Indeed, the Pb concentrations were considerably more elevated than in the TSP and MAP samples, as well as reporting higher than typical average concentrations for TSP (Guiffre de Lopez Carnelo, et al., 1997).

The TSP sample contains 21.4 % (w/w) P and a series of trace elements (TE) impurities (Tables S2 and S3). Of note the Cd concentration in the TSP was 23 mg kg⁻¹, whereas all the struvite products tested had levels less than 1 mg kg⁻¹. The MAP sample contains 22.9 % (w/w) P, which is 17% less than the theoretical P content of 26.9 % in monoammonium phosphate. Only small concentrations of TE's (<1 mg kg⁻¹) are present, and MAP contains less Mg, Ca, Al, Fe and Mn than any of the other fertiliser products (Fig. 2; See SI Table 3).

344 The ^{31}P SSNMR spectra of the struvite products all contain a resonance at $\delta(^{31}\text{P}) = 6.3\text{-}6.4$ ppm,
 345 assigned to struvite (Bak et al. 2000). The samples HEL, HER, AAM, and XIA contained a low
 346 concentration (1-2.4 %) of an impurity phase at $\delta(^{31}\text{P}) = -7.3$ ppm (Table 3), which was assigned
 347 to newberyite ($\text{Mg}(\text{HPO}_4) \cdot 3\text{H}_2\text{O}$) based on the chemical shift (Hunger et al. 2004).
 348 Two large resonances assigned to monocalcium phosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) were
 349 observed in the ^{31}P SSNMR spectrum of TSP at $\delta(^{31}\text{P}) = 0$ ppm and -4.5 ppm, along with a smaller
 350 resonance at $\delta(^{31}\text{P}) = 2.8$ ppm (6 %) assigned to hydroxyapatite ($\text{Ca}_5\text{OH}(\text{PO}_4)_3$) (Fig. S1) (Rothwell
 351 et al. 1980). Dittmarite was not identified by the ^{31}P SSNMR, most likely because it is very difficult
 352 to distinguish dittmarite from struvite in ^{31}P SSNMR due to very similar chemical shift values,
 353 $\delta(^{31}\text{P}) = 6.2$ ppm (Bak et al. 2000) and $\delta(^{31}\text{P}) = 6.35$ ppm (Kongshaug et al. 2000), respectively.
 354 The ^{31}P SSNMR spectrum of BER contained no resonance in the reported chemical shift range for
 355 berlinite, i.e. $\delta(^{31}\text{P}) = -24.5$ to -25.3 ppm (Bleam et al. 1989, Turner et al. 1986). The spectrum of
 356 the sample MAP consisted of one resonance with $\delta(^{31}\text{P}) = 1.0$ ppm, which is consistent with
 357 monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) (Fig. S1) (Turner et al. 1986).
 358
 359 The PXRD patterns of all struvite products (Fig. 3 and SI Fig. S3) correspond closely to the
 360 reference sample pattern for struvite (ICDD no. 01-077-2303) (Ferraris et al. 1986). Only a few
 361 impurities were identified by PXRD: the BER sample contained a series of reflections at $2\theta = 26.6$,
 362 36.6 , 42.5 , 50.2 , and 60.0° , which match with the aluminum phosphate berlinite (AlPO_4 , ICDD
 363 no. 01-079-6073) (Labeguerie et al. 2010), and the HER sample shows a strong reflection at $2\theta =$
 364 10.0° and a couple of weaker reflections at $2\theta = 18.8$ and 24.4° that match dittmarite
 365 ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, ICDD no. 00-020-0663) (Frazier et al. 1966).
 366 Furthermore, the HEL sample contains weak reflections at $2\theta = 18.7$ and 28.9 corresponding to
 367 newberyite ($\text{Mg}(\text{HPO}_4) \cdot 3\text{H}_2\text{O}$, ICDD no. 01-075-1714) (Bartl et al. 1983). These two reflections
 368 do not match struvite but could not unambiguously be assigned to newberyite, as reference PXRD

patterns of newberyite do not cover this 2θ range. The PXRD of TSP match monocalcium phosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, ICDD no.01-075-1521) (Jones and Cruickshank 1961) with a few reflections at $2\theta = 14.7$, 25.4 , and 25.6 belonging to basanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, ICDD no. 00-037-0246) (Lager et al. 1984). MAP contains only monoammonium phosphate from the PXRD pattern ($\text{NH}_4\text{H}_2\text{PO}_4$, ICDD no.01-072-4581) (Tenzer et al. 1958).

3.2 Fertiliser product solubilisation

H_2O extractable-P is ca. 10% higher in the chemical fertilisers compared with the struvites, yet conversely the HCl extractable-P was 15% lower (Fig. 4). The solubility of individual struvites, tested both by H_2O and HCl extractions, differed ($P < 0.001$, $P < 0.001$ respectively, Fig. 4). HCl extractable-P was 17% higher than H_2O extractable-P, resolving the struvites into seven groups as opposed to three (Tukey pairwise comparison, Fig.4). Struvite precipitation technology did not influence solubility (H_2O $P = 0.724$; HCl $P = 0.765$, see SI, Table S6.1).

Unplanted soil incubation experiments featuring all three soils used showed no difference between struvite fertilisers and TSP behaviour in soil solution at 4-weeks or 3-months. There was no significant difference between the struvites in any of the incubation experiments (GLM analysis, see SI, Table 6.1). There is, however, a difference in $^{\text{P}}C_{\text{DGT}}$ between the three soils ($P < 0.05$, Fig. 5). None of the extraction experiments correlate with shoot P offtake (H_2O $P = 0.120$; 1M HCl $P = 0.129$) or planted DGT soil samples (H_2O $P = 0.639$; 1M HCl $P = 0.461$). Although there is no relationship between the extractions and total P offtake in perennial ryegrass shoots, there is a strong relationship between incubated soil DGT measurements and DGT measurements in planted systems ($R^2 = 0.7$; $P < 0.001$), and between total P offtake in shoots and DGT measurements in planted systems ($R^2 = 0.80$; $P < 0.001$) shown in Fig. 6.

3.3 Experiments using Perennial Ryegrass

3.3.1 Experiment A.

There was no significant difference in shoot yield (GLM analysis $P = 0.436$), or P-offtake between the different struvite fertilisers and TSP/MAP (GLM analysis $P = 0.904$) (See SI 6.2-6.4). However, there were differences in the fertiliser dose effect ($P < 0.001$, Fig. 7), with higher P additions increasing growth/yield and P-offtake. The TSP dose response relationship, with five treatment levels showed a strong correlation with yield ($R^2 = 0.88$). Likewise, the individual struvite products showed a strong relationship between dose and P shoot offtake ($R^2 = \geq 0.99$ -1, Fig. 7). Overall, there is no difference between the struvite products used or any significant deviation in behaviour when compared to chemical fertilisers. There is no overall difference in DGT measured P ($^P C_{DGT}$) bioavailability of the struvite products and chemical fertilisers (GLM analysis $P > 0.305$). Similar to the directly observed plant trends, DGT detected a P dose effect for P offtake (GLM analysis $P < 0.001$; Fig. 8). However, this difference in P availability at different dose levels is not detected by Olsen-P (GLM analysis $P = 0.232$; Fig. 8).

3.3.2 Experiment B.

Shoot yield (GLM analysis $P = 0.130$), nor P-offtake (GLM analysis $P = 0.288$) did not differ between the different struvite fertilisers and TSP/MAP, across both soils (2 and 3, see SI). P-offtake values for soil 2 averaged 21 mg P and ranged from 19-24 mg P (Fig. 9). Soil 3 has significantly less P offtake with an average of 15 mg P (29% less than soil 2). The toxic metals Cr, Cd and Pb, that were found as impurities in the fertiliser samples (Fig. 2), their concentrations were checked in the harvested plant material. There were no detectable traces ($< LOD$) of these metals in shoot offtake.

${}^P\text{C}_{\text{DGT}}$ shows no difference between the fertiliser treatments, but a significant difference between soil 2 and 3 was detected (Fig. 9). In this experiment ${}^P\text{C}_{\text{DGT}}$ measurements correlate with P offtake (Fig. 7 and Fig. 8), which matches the trends of the 4-week trial (Exp. A), but the overall relationship was stronger ($R^2 = 0.65$; $P < 0.001$; Fig. 10). In contrast, Olsen-P showed no relationship with P offtake ($R^2 = 0.00$; $P = 0.984$; Fig. 10). ${}^P\text{C}_{\text{DGT}}$ and Olsen P did not correlate ($R^2 = 0.04$; $P = 0.197$).

3.4 Comparison of P bioavailability tests.

Olsen-P was found to be a poor predictor of plant P uptake across all experiments (Fig. 8). DGT, however, successfully estimated the plant requirements (Fig. 6f; Fig. 10). The range of DGT measured P spanned $1.2 - 179 \mu\text{g L}^{-1}$, which is comparable with other similar soil-P studies (See S6, SI). There is a highly significant linear relationship ($R^2 = 0.69$; $P = < 0.001$) between P availability measured by DGT in the unplanted and planted soil experiments (Fig. 6e) indicating a commonality in the supply of P in the two systems. However, ${}^P\text{C}_{\text{DGT}}$ in the unplanted soils only partially explains plant-P offtake ($R^2 = 0.48$; $P = 0.001$). Interestingly, the relationship between ${}^P\text{C}_{\text{DGT}}$ from the planted soils and plant-P offtake was better described using a hyperbolic model (Fig. 6) than a linear term, unlike the unplanted soils. This demonstrates two key points. Firstly, this biphasic characteristics in P assimilation with an inflexion point at ca. $20 \mu\text{g L}^{-1}$, is in keeping with our understanding of P transport into plants as explained by high and low-affinity uptake pathways (Meharg and Macnair, 1992), i.e. a plant regulated decrease in P uptake as P bioavailability increases. Secondly, the importance of the root-soil-fertiliser interaction.

4.0 Discussion

4.1 Struvite Speciation

Characterisation of the struvite products by SSNMR and PXRD showed that struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) was the dominating phase in all samples tested. Impurities such as newberyite ($\text{Mg}(\text{HPO}_4) \cdot 3\text{H}_2\text{O}$) only constituted 2.4 % of the P in the HEL product. Newberyite was the only impurity observed by SSNMR and was present in several of the ^{31}P SSNMR spectra of the struvite products, but was only detected by PXRD for a single sample. Other impurities such as the berlinite (AlPO_4) in the BER sample, and the dittmarite ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) in the HER sample, were only observed by PXRD. Hence, a combination of the two characterisation methods would appear necessary to gain a comprehensive understanding of P speciation in the struvite products. Berlinite was observed in PXRD of the BER sample, but the ^{31}P SSNMR spectrum contained no resonance in the reported chemical shift range for berlinite, i.e. $\delta(^{31}\text{P}) = -24.5$ to -25.3 ppm (Bleam et al. 1989, Turner et al. 1986). This discrepancy between the phases observed by SSNMR and PXRD is related to the basis of the two characterisation methods: PXRD identifies crystalline phases, whereas SSNMR differentiates between nuclei of a specific isotope with different local chemical environments in both crystalline and amorphous phase. Hence, if only a very small amount of crystalline berlinite is present, then the phase will be detected by PXRD but not necessarily by ^{31}P SSNMR.

The traditional granular chemical fertiliser TSP contained the phases expected: MAP was pure mono ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) from both PXRD and ^{31}P SSNMR, and TSP contained primarily MCPM ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) with 6 % of the P atoms bound in hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and some bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) identified by PXRD. As bassanite does not contain P, the presence of bassanite cannot be confirmed by ^{31}P SSNMR spectroscopy. Phosphate rock often contains high amounts of apatite (Desmidt et al. 2015) and is used as the basic material for TSP production, which explains the small amounts of unreacted hydroxyapatite in the TSP sample.

466 Newberyite and dittmarite are closely related to struvite, as they can both form from struvite
467 (Bhuiyan et al. 2008, Snow et al. 2014). Newberyite is a common side product during struvite
468 precipitation (Babić-Ivancić et al. 2006), and the ratio between struvite and newberyite is affected
469 by, e.g., initial pH (Ma et al. 2014) and N:P ratio in the liquid (Lu et al. 2016).

470 Dittmarite is a rare mineral that has been suggested to form in nature from struvite decomposition
471 in the presence of ammonia, NH_3 (Snow et al. 2014). Furthermore, dittmarite can form when
472 struvite is boiled in excess water (Bhuiyan et al. 2008, Sarkar 1991). Newberyite has also been
473 observed in urinary stones, where struvite commonly constitutes the majority of the mineral
474 content (Bak et al. 2000), as well as in poultry litter (Hunger et al. 2008). Both newberyite and
475 dittmarite are known to form in some cases when struvite is precipitated. Zhang and coworkers
476 observed newberyite precipitation along with struvite for synthetic brackish water, whereas
477 struvite precipitation from a digestate filtrate was accompanied by dittmarite precipitation. It was
478 suggested that a higher NH_4^+ concentration was the reason for dittmarite precipitation in the filtrate
479 and not in the synthetic brackish water (Zhang et al. 2016).

480 The presence of 2.4% of dittmarite in the HER sample is not expected to alter the bioavailability
481 of the struvite product, as dittmarite transforms into struvite when the compound comes in contact
482 with soil moisture (Bridger et al. 1962). This is further supported by a study of the plant availability
483 of dittmarite where dittmarite increased dry matter yields of spring wheat compared to the control,
484 just as struvite and TSP (Massey et al. 2009). However, the plant availability of newberyite has to
485 our knowledge not been investigated. Plus, the overall value of newberyite as a fertiliser is less
486 than struvite, due to the absence of ammonia. Hence precipitation of these phases is undesired.
487 Furthermore, excess Mg in the struvite product has been shown to decrease the P release (Degryse
488 et al. 2017), and this effect was ascribed to local pH changes in the soil near to the struvite particles,
489 which contained $\text{Mg}(\text{OH})_2$ as characterised by PXRD. Impurities like newberyite and dittmarite

are therefore not expected to decrease the P release from struvite fertilisers dramatically, when only present in these minute amounts.

The struvite products used in this study were generally characterised by having low metal impurity concentrations (1-8 mg kg⁻¹) containing significantly less Cd, Ni, Zn, and Cr than the TSP sample. The struvite products were characteristically different in Fe, Al, Ca, Cu, Zn, and Mn concentration, with BER, HER and HEL especially exhibiting higher metal levels compared to the other struvite products. This may be ascribed to differences in the technology used for struvite precipitation. The BER sample is precipitated directly in the sludge, which increases the incorporation of organic material and also some metals, whereas the rest of the samples have been precipitated from reject water from the digested sludge. The HEL and HER samples are precipitated by the same technology, Phosphogreen, as the Aaby samples (AAS, AAM, AAL), which are very low in metals. This could indicate that the relatively high metal content of HEL and HER is not caused by the processing technology, but rather factors such as operational set-up, or the composition of the influent wastewater. An interesting observation is that the composition of the struvite products from Aaby differ in metal composition dependant on the size of the struvite particles, which could indicate that operation of the struvite precipitation facility and the WWTP may have an effect. Even though the struvite products demonstrate small differences in metal content, they are still of a higher purity than TSP. Precipitated struvite products contain only trace concentrations of heavy metals (Li et al. 2019), which are considerably lower than that of the traditional commercially available granular inorganic fertilisers (Nziguheba and Smolders 2008) and were also undetectable in the plant XRF analysis.

4.2 Solubilisation of P. The different behaviours of the struvites and chemical fertilisers in H₂O/HCl-extractable P assays, are predictable, as struvite is scarcely soluble in water at around 1-

5% (Achat et al. 2014, Cabeza et al. 2011), but almost 100% soluble in acids (Ahmed et al. 2018). However, why there is differentiation in solubility between the individual struvite products is less obvious. The HEL struvite, which has the greatest dittmarite content at >2% along with relatively high concentrations of other elemental impurities, had a higher extractable P (4% H₂O; 7% HCl) than the purest struvite products XIA and CGL. However, higher concentrations of metal impurities alone (Fig. 2) did not directly relate to enhanced solubility (see BER and HER samples, Fig. 2), indicating a mixed mode of P-release.

4.3 Struvite in soil. DGT and Olsen-P tests showed that there was no difference in the overall bioavailability of the individual struvite products in Irish soils of the same soil-P index in both 4-week and 3-month experiments (Fig. 5; Fig. 8). Even in the soil of the lowest pH (4.8) there was no enhancement in the resolution/differentiation in behaviours between the struvites, unlike the extractable-P trends. Dissolution of P from struvite in soil is known to be modulated by pH, but P-bioavailability is dependent on pH as well as other soil characteristics that influence P fixation processes (Degryse et al. 2016; Penn and Camberato 2019). P retention mechanisms, for example anion and ligand exchange as well as precipitation of Fe and Al phosphates, can break the direct relationship between fertiliser solubility and bioavailability (Penn and Camberato 2019). In addition, the total P-bioavailability is not just a measure of fertiliser P supply but is comprised of a contribution from the soil. In our experiments, higher soil pH resulted in greater overall bioavailability of P from the soils (Fig. 8), which conflicts with struvite solubility trends (Fig. 4), and poses questions regarding the role of soil health and biota.

The soils featured in our experiments are typical of the north-east region of the island of Ireland. In addition to exhibiting a low pH, they are also enriched in Al and Fe, which means P bioavailability is generally low compared with the total P concentrations in the soils (Bell et al.

2005). Taking the 3-month experiment and $^P\text{C}_{\text{DGT}}$ measurements as an example, the background P supply (i.e. no P addition), measured from the low pH soil (soil 3 – pH 5.4) averaged $1.2 \mu\text{g L}^{-1}$, whereas in soil 2, with a pH of 6.2 it was nearly an order of magnitude higher at $11 \mu\text{g L}^{-1}$ (Fig. 6). However, the enhancement in additional P availability from the amendment of the soils with the same P fertiliser dose resulted in a 7-fold increase in soil 2 compared to soil 3 (Fig. 5). Further evidence, as to the importance of P-fixation within the soil as a control of bioavailability is presented when $^P\text{C}_{\text{DGT}}$ values in the unplanted soils are compared with the extractable P assays (Fig. 6). The DGT measurement integrates a number of important parameters involved in the bioavailability of P, such as P release of the soil, P reabsorption/fixation and fertiliser P dissolution. Based on understanding of P solubilisation of the struvites, dissolution would be greater in soil 3 because of the lower pH. However, this released P would be more effectively captured/retained by soil chemical processes, as a consequence of the lower pH. Furthermore, the stronger relationship (ca. R^2 0.70) between DGT and the extractable-P values from soil 2, when compared with soil 3 (R^2 0.34) demonstrate that when P bioavailability is higher, P solubilisation patterns play more of a role in defining bioavailability.

4.3 Struvite in planted systems. A major strength purported for struvite based products is that their fertiliser effect is root activated and hence P release originates in zones within in the soil that have a nutrient requirement. Similar to the unplanted soils, P availability did not differ in the perennial ryegrass experiments between the struvites and the chemical fertilisers. Although the soil-root interactions within the experiments did not differentiate between the different struvites, there was an overall enhancement of P bioavailability because of the plants. Using again, the examples of soil 2 and 3, the DGT measurement of P shows that P bioavailability increases between 10-20% (see SI). This is despite considerable P removal by the plants themselves, which would exhaust some of the P supply within the soil. Interestingly, in the soil with the lowest pH the gain in P

bioavailability as a proportion of P release in the unplanted soil, was double that of the higher pH soil.

The European Commission are revising regulations governing struvite, which will impact on how waste-recovered fertilisers are categorised (Huygens et al., 2018b). Part of this revision process is to CE-mark certify the recycled products based on their manufacturing/processing technologies and waste materials used (Huygens et al., 2018b). The primary advantage this affords, is that the waste status of the recovered product ceases to exist. This makes it easier for recycled materials to be blended, but also confers benefits related to reducing hazard risk and improving product consistency (Huygens et al., 2018b). Using a range of bioavailability/growth tests we have found that not only is struvite as effective as chemical fertiliser, but when amended within Irish soils it gives a uniform response. This provides further evidence that the struvites from different waste sources and precipitation technologies can demonstrate P conformity, despite differences in physical appearance. The caveat to this though, is that P solubilisation from struvite has been shown to be influenced by particle size (Degryse et al. 2017), so a classification scheme for struvites that takes into account form, size and morphology would be beneficial. The impact of particle size within Irish soils remains to be determined.

5.0 Conclusions

The struvite products generated from different wastewaters and processes do vary in physical appearance and metal impurities, but they do possess uniformity in P speciation (SSNMR, PXRD) and overall fertiliser performance, as demonstrated in our plant experiment trials. Other recovered P fertilisers can be produced from WWTP processes, such as sludge biochar, however, they can provide highly variable yield responses when applied to soil (Glaser and Lehr, 2019).

Encouragingly, no appreciable agronomic differences were observed between the struvite and chemical fertilisers, which provides further evidence for struvite as a sustainable alternative to mined rock phosphate. Furthermore the struvite products generally contain lower concentrations of metal contaminants, such as Cd. However, Pb levels should still be monitored in some struvites.

Olsen-P is the sector standard for soil P analysis and is currently widely used for calculating soil P indices. However, plant utilisation of P from struvite amended soils was successfully predicted by ${}^P\text{C}_{\text{DGT}}$ ($R^2 = 0.8$) but not Olsen-P. The DGT measurement integrates parameters such as struvite solubility along with soil re-adsorption processes more effectively than its chemical counterpart (Fig. 6). Struvite offers an opportunity to recover P and potentially improve agricultural P use efficiency. However such gains will not be fully realised in Irish soils under current soil testing methodology, nor will it be, if root activated fertilisers are tested and evaluated in systems that do not have the capacity to account for root-soil-fertiliser interactions.

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Table 1: Overview of the fertiliser products characterised in this study. All samples were ground and sieved to give a particle size of $\leq 2\text{mm}$.

Material	Abbreviation	Source	Struvite technology
Triple super phosphate	TSP	Triple super phosphate from Goulding Fertiliser NI.	-
cleanMAP®	MAP	Mono ammonium phosphate recovered from wastewater sludge ash by the company Easymining	
Chinese struvite	XIA	Struvite from anaerobically digested swine waste water in Xiamen, China	Struvite precipitation by stirred reactor (Chen et al. 2017, Chen et al. 2018)
Crystal Green® small and large	CGS CGL	Commercially available struvite from Ostara in small (1.5 mm) and large (3 mm) pellets.	PEARL
Aaby small, medium and large	AAS AAM AAL	Struvite from full-scale struvite production at Aaby WWTP, Aarhus Vand, Denmark in small (1 mm), medium (2 mm) and large (3 mm) pellets.	Phosphogreen
Herning	HER	Struvite from full-scale struvite production at Herning WWTP, Herning Vand, Denmark	Phosphogreen
Helsingør	HEL	Struvite from full-scale struvite production at Helsingør WWTP,	Phosphogreen
Berliner Pflanze®	BER	Commercially available struvite from a full-scale struvite production from Berliner Wasserbetriebe.	Airprex

Table 2: Overview of soil characteristics

	Soil 1	Soil 2	Soil 3
American soil classification	Gray-brown	Gray-brown	Humic-gley soil
system 1938	podzolic soils	podzolic soils	
Texture	Sandy clay loam	Sandy clay loam	Organic sandy texture
pH	4.8	6.2	5.4
Total P (mg/g)	0.7	2.3	1.7
Total Al (mg/g)	74	81	70
Total Fe (mg/g)	32	33	31
Total Mg (mg/g)	11	14	13
Total Ca (mg/g)	2	3.5	2

Table 3: Overview of phase composition of fertiliser samples from ^{31}P MAS SSNMR and PXRD. Chemical shift ($\delta(^{31}\text{P})$) and integral (I) of SSNMR resonances are given. Phases are indicated by their names: Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), Newberyite ($\text{Mg}(\text{HPO}_4) \cdot 3\text{H}_2\text{O}$), Berlinite (AlPO_4), Dittmarite ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$), Bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), Monocalcium phosphate monohydrate (MCPM, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), and monoammonium phosphate (MAP, $\text{NH}_4\text{H}_2\text{PO}_4$). Estimated uncertainties are given in brackets. * not detected in PXRD.

Sample	Phase(s)	$\delta(^{31}\text{P})$ (ppm)	I (%)	Comments
TSP	MCPM	-4.5	48(1)	Bassanite (PXRD)
		0.0	46(1)	
	Hydroxyapatite*	2.8	6(1)	
MAP	MAP	1.0	100	
XIA	Struvite	6.4	100(1)	
	Newberyite*	-7.3	0(1)	
CGS	Struvite	6.3	100	
CGL	Struvite	6.3	100	
AAS	Struvite	6.3	100	
AAM	Struvite	6.4	100(1)	
	Newberyite*	-7.3	0(1)	
AAL	Struvite	6.3	100	
HER	Struvite	6.4	99(1)	Dittmarite (PXRD)
	Newberyite*	-7.3	0.6(10)	
HEL	Struvite	6.4	97.6 (10)	
	Newberyite*	-7.3	2.4 (10)	
BER	Struvite	6.3	100	Berlinite (PXRD)

Figures

Figure 1: Struvite products investigated in this study.

Figure 2. Elemental Characteristics of P Fertilisers. a) Radar chart of the TSP control and mono-ammonium phosphate (MAP) fertilisers and BER struvite. b-c) Radar charts of the struvite fertilisers by different production technologies. Analysis was undertaken by ICP-OES. Radar charts show percent. 100% is calculated as the highest reading for any respective element in a.), 100% for each element is respective to % of P) 22.9, Mg) 10.8, Al) 0.20, Fe) 0.30, Ca) 18.71, Cu) 0.01, Cr) 0.013, Cd) 0.002, Zn) 0.05, Ni) 0.003 Pb) 0.001, Mn) 0.02. b-c) 100% is calculated as the highest reading for any respective element in the WRS from Pearl, swine manure and Phosphogreen. 100% for each element in b-c) is respective to % of P) 13.6, Mg) 10.8, Al) 0.015, Fe) 0.3, Ca) 0.11, Cu) 0.0006, Mn) 0.002.

Figure 3: ^{31}P solid state NMR spectra and PXRD patterns of selected struvite products. a) SSNMR of CGL, b) SSNMR of BER, c) SSNMR of HER, d) SSNMR of HEL, e) PXRD for CGL, f) PXRD for BER, g) PXRD for HER, and h) PXRD for HEL. SSNMR: The spectra were recorded at 202.4 MHz with 15 kHz spinning. PXRD reflections from impurities are marked with • (Berlinite), ○ (Dittmarite), and ◇ (Newberyite). Additional SSNMR and PXRD data for the other samples can be found in supporting information.

Figure 4: Extractable P measured from chemical solubility assays. a) H₂O extraction ($P < 0.05$), b) 1M HCl extraction ($P < 0.001$). P-values in parentheses are from GLM analysis (struvite products only), letters (A-F) within the figure refer to different grouping from Tukey pairwise comparisons. Coloured groupings denote general fertiliser type based on struvite precipitation technologies.

Figure 5: $^{PC}_{DGT}$ results from the three used soils after incubation without plants for 4 weeks (soil 1) and 3 months (soils 2 and 3). GLM analysis on all the unplanted soils show there is no difference in $^{PC}_{DGT}$ in the unplanted soils between the struvite treatments.

Figure 6: Fertiliser-Soil-Plant Relationships. Panels a-d: Correlations between water-extractable or acid-extractable P and soil $^{P}C_{DGT}$ in incubated unplanted soil for a-b) soil 2 (control 11 $\mu\text{g/L}$), c-d) soil 3 (control 1.2 $\mu\text{g/L}$), e.) Planted and unplanted $^{P}C_{DGT}$ infinite sink correlation, f) soil $^{P}C_{DGT}$ and total P offtake in planted systems in 50 kgP/Ha addition (experiments A and B combined.)

Figure 7: P offtake (mg/P), calculated as total P in shoot dry matter per Ha, over a 4-week growth trial (experiment A). a. Total P in each soil column per treatment, b. linear regression of dose effect for each fertiliser treatment (TSP $R^2 = 1$, MAP $R^2 = 0.99$, XIA $R^2 = 1$, CGL $R^2 = 0.99$, AAS $R^2 = 0.99$, HER, $R^2 = 0.99$, BER $R^2 = 0.99$). *CI.* Dotted line indicates the 95 % confidence interval of the TSP and MAP.

Figure 8: P bioavailability assays in planted systems, a) P offtake for shoot dry matter in experiment A, b) Soil P_{CDGT} in experiment A, c) Soil Olsen P in experiment A, d) P offtake in shoot dry matter in experiment B, e) Soil P_{CDGT} in experiment B, and f) Soil Olsen P in experiment B. Asterisks represent statistical difference in dose/soil

Figure 9: Total P (P offtake) calculated as total P in shoot dry matter per pot over a 3-month growth trial (experiment B). Dotted line indicates P offtake in control treatment of soil 2 and 3 with no P addition (10g, 8g respectively). No statistical difference is observed between the treatments ($P = >0.1$). Soil 2 and 3 statistically different ($P = 0.001$).

Figure 10: Correlation between P offtake and soil bioavailability tests for the 3-month growth trial (experiment B). a. Olsen P and Plant P offtake ($P = >0.05$) b. PC_{DGT} and Plant offtake ($P = 0.0001$).

Supporting Information

Phosphorus speciation and fertiliser performance characteristics: a comparison of waste recovered struvites from global sources

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S1. Characteristics of recovered fertilisers.

The fertilisers used in this study were struvite products precipitated at wastewater treatment plants in Denmark (Herning, Aaby, and Helsingør), from pig slurry in China (Xiamen) (Chen et al. 2017, Chen et al. 2018), along with commercially available struvite products from Berliner Wasserbetriebe (Berliner Pflanze™) and Ostara (Crystal green™). At Aaby wastewater treatment plant, three different sizes of struvite pellets were produced: 1 mm, 2 mm, and 3 mm. Triple super phosphate (TSP), a commonly used inorganic P fertiliser, was used for comparison and for establishing the growth response relationship in the plant experiments between soil and P doses. A highly soluble monoammonium phosphate reclaimed from sewage sludge ash (cleanMAP®, EasyMining, abbreviated MAP) was included as a water-soluble, waste recovered P fertiliser. The struvite products can be seen in figure 1 and are described in table 1. The struvite products are referred to by these abbreviations: Herning (HER), Aaby small (AAS), Aaby medium (AAM), Aaby large (AAM), Helsingør (HEL), Xiamen (XIA), BerlinerPflanze™ (BER), Crystal green 1.5 mm (CGS), and Crystal green 3 mm (CGL).

S2. Plant Experiments

Experiment A. The fertiliser effect of the struvite products was tested in a highly controlled short-term (4 week) experiment with ryegrass, to investigate fertiliser performance in NI soils across a range of amendment doses (25, 50 and 100 mg P/hectare). Early stage rhizosphere formation was induced in homogenously packed soil columns (250g soil; 10cm x 6.8cm), by transplanting a standardised seedlings biomass (ca. 25 plants, 4 replicates of each treatment) to create a uniform environment to isolate plant-soil-fertiliser interactions.

Ryegrass seeds were germinated on rock wool in a hydroponic growth system in a greenhouse, and after a month the seedlings were transplanted into soil-filled pots amended with different

fertilisers and then grown in a controlled environment growth chamber for four weeks. Perennial Ryegrass (AberMagic high sugar diploid: Morton's, Hillsborough) was germinated in rockwool-supported hydroponics system (Växer from IKEA) in a greenhouse using a ¼ strength Hoagland solution (Supporting information page S3). 2g (wet weight) of healthy seedlings were removed from the hydroponic system at four weeks and used for transplanting.

The recommended P fertiliser level for grass establishment on NI soils with P-index 0 (Olsen-P 0-9 mgP/kg soil) is 120 kg P₂O₅/ha, corresponding to 52.3 kgP/ha (AHDB 2018). struvite products and clean MAP were ground and added at three levels: The recommended level (50 kgP/ha, corresponding to 73 mgP/(kg dry soil)), a low level (25 kgP/ha, corresponding to 36 mgP/(kg dry soil)) and a high level (100 kgP/ha, corresponding to 146 mgP/(kg dry soil)). Ground TSP was added at five levels and served as a control response curve with the following doses: 0 kgP/ha, 12.5 kgP/ha, 25 kgP/ha, 50 kgP/ha, and 100 kgP/ha. The fertilisers were dosed based on their total P content to ensure that all pots received the same amount of total P.

Each soil batch was prepared in the same way: 250 g of dry soil (sieved to <2mm) was mixed with a corresponding addition of P fertiliser (Table S1), along with a replete supply of N in the form of 125 mg urea. N dosing was undertaken to standardise the experimental conditions and to isolate the impact of P uptake by the plants. Soils were shaken using a VWR Multi-Tube Vortexer for 10 min and wetted to 65% WHC, the soil was then incubated for four days and packed to a bulk density of ~1.3 g/cm³ in the cylindrical PVC soil columns (washed in 7% nitric acid). Planted soil columns were watered every 5/7 days and kept at 65% WHC using a capillary action watering method throughout the 4 week growth period.

The controlled environment growth chamber was kept at 20°C with a 16 hour day-light period. Each planted pot had 4 replicates in a randomised block design, with pots in each block rotated every 5/7 days. An additional pot without plants was watered alongside the planted treatments throughout the growth period to provide information on only soil chemistry/solubility between treatments in the absence of plants.

Grass samples were harvested by cutting the plant shoot and dried at 65°C until completely dry. Dry Matter (DM) yields were then obtained by weighing the dried shoot material. Plant shoots were then ground at 500 rpm for 5-8 minutes in a Retsch PM100 ball mill using porcelain grinding equipment.

Table S1a. Fertiliser addition to each soil column
(Experiment A)

Fertiliser Treatment	Total P (mg/g) ICP-OES	Low dose (g)	Medium dose (g)	High dose (g)
TSP	213	0.0427	0.0855	0.1709
MAP	275	0.0332	0.0664	0.1327
XIA	135	0.0673	0.1346	0.2693
CGL	131	0.0694	0.1388	0.2776
AAS	134	0.0682	0.1364	0.2727
HER	129	0.0709	0.1418	0.2835
BER	90	0.1013	0.2027	0.1709

Table S1b. Fertiliser addition to each soil pot (Experiment B)

Fertiliser Product	Total P (mg/g) ICP-OES	Medium Dose (g)
TSP	213	1.71
MAP	275	1.33
XIA	135	2.69
CGL	131	2.78
AAS	134	2.73
HER	129	2.84
BER	90	4.05

Figure S1. Photos of plant Experiment A. a-b. Day 1 in growth chamber, c. Week 2 in growth chamber, d. week 4 in growth chamber.

Experiment B. The 4-week screening experiment was followed-up by a 3 month greenhouse/pot trial (5 kg soil; 30cm x 25cm, n=3) where the different struvites were interrogated using two NI soils of different pH (BE3M: 6.2 and MG3M), to consider plant growth over longer timeframes.

Soils were treated with a fertiliser dose of 50 kgP/ha and equivalent N (Urea). BE3M was treated with the same fertilisers as the 4-week ryegrass experiment (No P addition, TSP, MAP, XIA, CGL, AAS, HER, BER) where MG3M was only treated with commercially available fertilisers TSP, XIA, CGL, BER and a control treatment with no P addition. Fertilisers were applied to the top layer of soil and then mixed by hand to get a homogeneous distribution. Soils were left to equilibrate for four days after and kept at 65% WHC throughout the experimental procedure, ryegrass germination experimental procedures from the 4-week screening were followed with 20g of wet biomass transferred into the soil (sieved <2mm). A growth period of 3 month was carried out with assisted heat lighting from 8am-8pm. Ryegrass shoots and soils were harvested and treat with same protocol from experiment A.

Figure S2. Photos of plant Experiment B. a. Day 1 in greenhouse, b. Week 2 in greenhouse, c. week 3 in greenhouse, d-e. week 9 in greenhouse, f. week 12 in greenhouse.

Table S2. Comparison of Experiment A and B

	Experiment A	Experiment B
Objective	Fertiliser performance across a range of amendment doses (25, 50 and 100 kg P ha ⁻¹).	Plant growth and plant-soil-fertiliser interactions over a longer time using two soils of different pH (Soil 2: 6.2/Soil 3: 5.4)
Duration of experiment	4 weeks	3 month
Environmental conditions	Controlled environment growth chamber	Greenhouse with heat lamps
Soils used	Soil 1: Brown Earth, pH 4.8	Soil 2: Brown Earth, pH 6.2 Soil 3: Mineral Gley, pH 5.4
Pot size/soil weight	250g soil; 10cm x 6.8cm, n=4	5 kg soil; 30cm x 25cm, n=3
Seedling Biomass transfer	2g wet biomass	20g wet biomass
Watering regime	5/7 days (65% WHC)	2/7 days (65% WHC)

S3. Nutrient solutions for hydroponic nursery systems

A) 812 mM KNO₃, 500 mM Ca(NO₃)₂·4H₂O.

B) 250 mM NH₄H₂PO₄, 250 mM MgSO₄·7H₂O.

C) 4.6 mM H₃BO₃, 0.5 mM MnCl₂·4 H₂O, 0.2 mM ZnSO₄·7H₂O, 0.1 mM (NH₄)₆Mo₇O₂₄·4H₂O, 0.2 mM CuSO₄·5H₂O. D) 45 mM NaFeEDTA.

For each 5 L of diluted Hoagland, 10 mL of A, 10 mL of B, 1.25 mL of C, and 1.25 mL of D were used. This means that the diluted Hoagland solution that was used for the plants consisted of: 1.625 mM KNO₃, 1.0 mM Ca (NO₃)₂·4H₂O, 0.5 mM NH₄H₂PO₄, 0.5 mM MgSO₄·7H₂O, 1.15 μM H₃BO₃, 0.125 μM MnCl₂·4 H₂O, 0.05 μM ZnSO₄·7H₂O, 0.025 μM (NH₄)₆Mo₇O₂₄·4H₂O, 0.05 μM CuSO₄·5H₂O, 11.25 μM NaFeEDTA.

Nutrient solution applied first on day 8 (13th Oct) after seeding (5th Oct) and then changed every four-six days (17th, 23th and 27th Oct). The stock solutions were made from distilled water, dilution made with tap water.

S4. Elemental analysis

In order to determine the P content of the struvite products for dosing of struvite in the plant experiment, and to investigate the metal composition of the struvites, elemental analysis by was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2100 DV). Total P and metals were measured on fertiliser samples which had been microwave digested in concentrated HNO₃ (0.1 g sample in 6 mL HNO₃). The samples were measured in radial mode at the following wavelengths: Al (396.153 nm), Ca (317.933 nm), Cd (228.803 nm), Cr (267.716 nm), Cu (327.393 nm), Fe (238.204 nm), Mg (285.213 nm), Mn (257.610 nm), Ni (231.604 nm), P (213.617 nm), Pb (220.353 nm), Zn (206.200 nm). SCP science PlasmaCAL Water and Wastewater (Alternate metals I, II) were used for quality control.

³¹P magic angle spinning solid state NMR spectroscopy. Solid state ³¹P NMR spectroscopy was performed at 11.7 T on a 500 MHz Jeol ECZ 500R spectrometer with a 3.2 mm Jeol MAS NMR probe. Quantitative ³¹P MAS NMR spectra (45° flip angle) were recorded for all fertiliser samples with 15 kHz magic angle spinning (MAS). The carrier frequency was set at -9 ppm. The recycle delay was optimized for each sample and set to 5·T₁ for the P signal in the sample with longest relaxation, as determined from inversion recovery experiments. Typical recycle delays chosen were 130-800 seconds. Spectra were referenced to H₃PO₄ (δ(³¹P) = 0 ppm), and single-pulse ³¹P SSNMR spectra were analysed by absolute integration of the resonances in MestReNova after baseline correction. When spinning side bands were present, they were included in the integration of the signals.

Powder X-Ray diffraction. PXRD diffractograms were recorded on a Rigaku Miniflex 600 diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The data were recorded in the range $2\theta = 3\text{-}90^\circ$ with a step size of 0.02 and a speed $10^\circ/\text{min}$. The software PDXL2 from Rigaku was used to match diffractograms with the ICDD library.

S5 Elemental composition of fertiliser samples

Table S2: P and Mg concentrations in the fertiliser samples (%) as measured by ICPOES. Standard deviation in parenthesis.

Sample	P	Mg
TSP	21.4(0.2)	0.5(0.0)
HER	13.2(0.5)	10.5(0.4)
AAS	12.2(1.6)	10.0(1.6)
AAM	13.6(0.04)	11.0(0.1)
AAL	13.5(0.1)	10.7(0.03)
CGL	13.4(0.5)	10.3(0.4)
CGS	13.2(0.2)	10.8(0.2)
XIA	12.6(0.4)	10.7(0.5)
BER	9.0(0.2)	7.7(0.1)
HEL	10.9(0.04)	9.5(0.2)
MAP	22.9(3.2)	0.0(0.0)

Table S3: Metal concentrations (mg/kg) as measured by ICP-OES, numbers in parenthesis are standard deviation. Samples were measured by microwave digestion in concentrated HNO₃ (0.1 g sample in 6 mL HNO₃).

Sample	Al	Fe	Ca	Cu	Cr	Cd	Zn	Ni	Pb	Mn
TSP	2001(19)	1031(18)	187063(97)	35(0.8)	131(0.7)	23(0.2)	502(8)	38(0.1)	<1	21(0.03)
HER	33(1)	1349(8)	1063(43)	3(0.5)	3(0.5)	<1	14(0.3)	<1	<1	196(8)
AAS	<1	215(24)	246(31)	1(0.1)	3(0.4)	<1	2(0.4)	<1	<1	48(7)
AAM	<1	99(0.4)	708(6)	<1	3(0.01)	<1	<1	<1	<1	18(0.1)
AAL	<1	120(0.5)	599(4)	<1	3(0.1)	<1	<1	<1	<1	51(1)
CGL	<1	208(9)	646(40)	<1	3(0.02)	<1	<1	<1	<1	12(0.4)
CGS	<1	290(11)	553(0.2)	<1	3(0.3)	<1	<1	<1	<1	12(0.1)
XIA	2(2)	10(3)	1096(49)	<1	3(0.1)	<1	1(0.05)	1(0.1)	<1	8(0.3)
BER	432(6)	2993(141)	6823(77)	55(12)	5(0.5)	<1	90(3)	5(3)	14(5)	96(5)
HEL	151(34)	746(25)	825(93)	6(1)	3(0.5)	<1	17(3)	<1	<1	35(2)
MAP	2(3)	5(0.4)	70(0.7)	3(0.7)	6(0.8)	<1	1(2)	<1	<1	<1

S6. ^{31}P SSNMR spectra of fertiliser products

Figure S3: ^{31}P MAS SSNMR spectra of fertiliser samples. ^{31}P MAS SSNMR spectra for samples CGL, HER, HEL, and BER can be found in the main article.

S7. PXRD data for struvite products

Figure S4: PXRD of struvite products. All match reference pattern for struvite (ICDD no. 01-077-2303). PXRD data for samples CGL, HER, HEL, and BER can be found in the main article.

S8 PXRD data for TSP and cleanMAP

Figure S5: PXRD for the TSP and MAP samples, which match reference pattern for $\text{CaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (ICDD no. 01-075-1521) and $\text{NH}_4\text{H}_2\text{PO}_4$ (ICDD no. 01-072-4581), respectively. Asterisks indicate reflections from the impurity basanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, ICDD no. 00-037-0246).

Figure S7: Biomass (g) response to fertiliser dose (kgP/ha) for different fertiliser products. R^2 values: 0.88 (TSP), 0.99 (MAP), 0.02 (HER), 0.97 (AAS), 0.96 (BER), 0.99 (CGL), 0.69 (XIA).

Table S4: Nutrient content of harvested plant material from ICP-OES analysis.

Amendment KgP/Ha		N		P		K		Ca		Mg		S	
	0	3.89	(0)	0.13	(-0.01)	1.8	(0.09)	0.27	(0.03)	0.2	(0.02)	0.29	(0.01)
TSP	12.5	3.76	(0)	0.16	(0.02)	1.63	(0.19)	0.295	(0.02)	0.2	(0.02)	0.28	(0.04)
	25	3.72	(0)	0.19	(0.02)	1.56	(0.11)	0.318	(0.03)	0.2	(0.01)	0.28	(0.02)
	50	3.62	(0)	0.24	(0.02)	1.34	(0.13)	0.329	(0.03)	0.2	(0.01)	0.27	(0.03)
	75	3.5	(0)	0.24	(0.01)	1.27	(0.04)	0.308	(0.04)	0.2	(0.02)	0.24	(0.03)
	100	3.81	(0)	0.35	(0.03)	1.34	(0.17)	0.346	(0.01)	0.2	(0.01)	0.3	(0.04)
MAP	25	4.03	(0)	0.21	(0.01)	1.66	(0.15)	0.321	(0.01)	0.2	(0.01)	0.3	(0.04)
	50	4.05	(0)	0.28	(0.02)	1.42	(0.05)	0.282	(0.04)	0.2	(0.01)	0.27	(0.01)
	100	3.86	(0)	0.35	(0.04)	1.23	(0.03)	0.265	(0.02)	0.2	(0.03)	0.24	(0.02)
HER	25	3.73	(0)	0.19	(0.01)	1.39	(0.03)	0.286	(0.05)	0.3	(0.02)	0.25	(0.02)
	50	3.82	(0)	0.25	(0.03)	1.41	(0.14)	0.301	(0.03)	0.3	(0.03)	0.25	(0.01)
	100	4.05	(0)	0.38	(0.05)	1.33	(0.16)	0.276	(0.02)	0.3	(0.02)	0.25	(0.05)
AAS	25	3.76	(0)	0.21	(0.03)	1.48	(0.15)	0.312	(0.04)	0.3	(0.02)	0.27	(0.03)
	50	4.08	(0)	0.25	(0.06)	1.45	(0.13)	0.284	(0.04)	0.3	(0.03)	0.27	(0.03)
	100	4.11	(0)	0.37	(0.04)	1.32	(0.23)	0.288	(0.03)	0.3	(0.04)	0.28	(0.05)
BER	25	3.57	(0)	0.17	(0.02)	1.41	(0.16)	0.298	(0.01)	0.2	(0.01)	0.25	(0.03)
	50	3.88	(0)	0.24	(0.04)	1.33	(0.24)	0.26	(0.04)	0.3	(0.02)	0.24	(0.04)
	100	3.81	(0)	0.35	(0.06)	1.17	(0.1)	0.278	(0.03)	0.3	(0.03)	0.22	(0.02)
CGL	25	3.89	(0)	0.19	(0.01)	1.61	(0.15)	0.308	(0.02)	0.3	(0.01)	0.29	(0.03)
	50	3.82	(0)	0.22	(0.01)	1.36	(0.06)	0.282	(0.02)	0.3	(0.01)	0.25	(0.01)
	100	3.76	(0)	0.27	(0.07)	1.23	(0.12)	0.278	(0.03)	0.3	(0.04)	0.25	(0.02)
XIA	25	3.85	(0)	0.19	(0.01)	1.44	(0.05)	0.292	(0.02)	0.2	(0.01)	0.25	(0.01)
	50	3.8	(0)	0.25	(0.03)	1.34	(0.18)	0.287	(0.03)	0.3	(0.02)	0.24	(0.03)
	100	3.96	(0)	0.37	(0.03)	1.27	(0.15)	0.282	(0.01)	0.3	(0.01)	0.24	(0.03)

Table S4.1: Nutrient quality control from XRF analysis (Experiment B). CRM used to calculate % recovery and Limit of detection (LOD) provided by Cartesian internal calibration. Plant CRM supplied from Institute of nuclear chemistry (Code: INCT-MPH-2) and Soil CRM supplied from International soil-analytical exchange (ISE) (Code: Soil ISE 921).

	Recovery Polish Mixed Herb %	Recovery Soil ISE 921 %	Limit of detection (mg kg ⁻¹)
P	85	111	15
Mg	113	118	1
Al	125	125	1
Fe	85	102	1
Ca	85	102	2
Cu	108	103	1
Cr	-	-	1
Cd	-	-	2
Zn	105	111	1
Ni	120	104	1
Pb	102	115	1
Mn	92	107	1

Figure S8. PCA of dry shoot matter nutrient analysis by ICP-OES. Nutrient content of harvested plant material from ICP-OES analysis available in supporting information.

S9. Quality control for the colorimetric measurements of phosphate

Olsen P and DGT measurements of plant available P - quality control. Quality control for the Murphy and Riley molybdenum blue reagent standard solutions used for calibration were potassium phosphate monobasic (KH_2PO_4), ammonium phosphate monobasic ($\text{NH}_4\text{H}_2\text{PO}_4$) and phosphate standard for ion chromatography (IC) solution. All standard solutions were supplied by Sigma Aldrich and compared to a synthetic surface water certified reference materials (CRM, SPS-SW2) supplied by Spectra Pure Standards of $500 \mu\text{g P L}^{-1}$. A calibration was conducted before a microplate was run on any individual period, after every three microplates had been analysed another calibration of $\text{NH}_4\text{H}_2\text{PO}_4$ was performed to check the quality of the reading (Table S4). All samples were analysed in random order and each sample had three analytical replicates.

Table S5: Quality control for the Murphy and Riley Molybdenum blue reagent standard solutions used for calibration were Potassium phosphate monobasic (KH_2O_4), ammonium phosphate monobasic ($\text{H}_6\text{NO}_4\text{P}$) and Phosphate standard for IC solution. All standard solutions were supplied by Sigma Aldrich and compared to a synthetic surface water CRM (SPS-SW2) supplied by Spectra Pure Standards of 500 $\mu\text{g/L}$.

Reference	Olsen P			DGT		
	LOD	R^2	% Recovery	LOD	R^2	% Recovery
Material	$\mu\text{g/L}$		(From CRM)	$\mu\text{g/L}$		(From CRM)
KH_2O_4	1	0.99	97	1	0.99	97
$\text{H}_6\text{NO}_4\text{P}$	1	0.99	97	1	0.99	97
IC	1	0.99	97	1	0.99	97

SI0. Calculation of DGT measured P bioavailability

DGT works by using a binding layer acting as an infinitive sink to accumulate solutes, overlain by a hydrogel and filter (well defined diffusion layer), and a diffusion boundary layer (DBL) to reach a steady state concentration gradient. To calculate flux, F , and the concentration of solute in the binding layer, C_{DGT} , (eq. 1-3);

$$F = \frac{M}{At} \quad (1)$$

$$C_{DGT} = \frac{(M-M')(\Delta g + \delta)}{DA(t-t')} \quad (2)$$

Where, M , is the mass of analyte from binding layer, t , is exposure time, A , is the exposure window of the surface gel (Davidson and Zhang, 1994). D , being the diffusion coefficient (provided by DGT Research LTD for each analyte), Δg is the diffusion layer thickness, δ , is the DBL in solution, t' and M' , is the time of establishing the concentration gradient and the mass of the DBL respectively. For successful deployment of the device in solution the steady state concentration gradient in the DBL needs to be established within seconds, therefore the t' and M' are negligible (Davidson and Zhang, 1994, Zhang and Davidson, 1998, Davidson and Zhang, 2008) and can be simplified by equation 3 (Ding et al., 2010).

$$C_{DGT} = \frac{M\Delta g}{DA t} \quad (3)$$

Using FeOH as a binding agent provides a specific strong affinity for immobilising P in soils, sediments and fresh water and has no biochemical interference with other ions. The capacity of Ferrihydrite impregnated gels is $\leq 400 \mu\text{g L}^{-1}$ (Ding et al. 2010). Table SI shows an example of DGT

measurements in soils.

Table S6. DGT measurements in soils

Soil	$P_{C_{DGT}}$ (μgL^{-1})	Reference
Performance of DGT in tropical soils	4.5-440	Six et al (2012)
35 field trials across Southern Australia and amended with TSP	10 - 232	Mason et al. (2010)

S11. Statistical Analysis Summary

S7.1 Fertiliser Product solubilisation

	Degrees of Freedom	Adjusted Means square	F	P
Struvite in HCl	3	4.2761	0.39	0.00
Struvite in HCl x Precipitation Process	3	15.9	0.03	0.765
Error	23			
Struvite in H ₂ O	8	6.000	3.24	0.027
Struvite in H ₂ O x Precipitation Process	3	1.598	0.44	0.724
Error	23			
Solubilisation	14.953	3.738	2.45	0.081
Soil type	7	70.1	5.74	0.003
Error	19			

S7.2 Experiment A

All treatments

	Degrees of Freedom	Adjusted Means square	F	P
P offtake				
Treatment	6	0.3335	2.05	0.072
Dose	2	32.8466	201.96	0.000
Treatment x Dose	12	0.0820	0.50	0.904
Error	82			
DGT				
Treatment	6	0.001064	1.23	0.305
Dose	2	0.040348	46.50	0.000
Treatment x Dose	12	0.001144	1.32	0.232
Error	62			

S7.3 Without TSP/MAP

	Degrees of Freedom	Adjusted Means square	F	P
P offtake				
Treatment	4	0.4340	2.35	0.068
Dose	2	24.6253	133.63	0.000
Treatment x Dose	8	0.1102	0.60	0.774
Error	45			
DGT				
Treatment	4	0.000828	0.87	0.490
Dose	2	0.027261	28.63	0.000
Treatment x Dose	8	0.000948	1.00	0.453
Error	25			

Experiment B

S7.3 All fertiliser treatments

	Degrees of Freedom	Adjusted Means square	F	P
P offtake				
Treatment	7	22.6	1.31	0.288
Soil	1	325	18.87	0.004
Treatment x Soil (1&2)	4	46.4	0.63	0.703
Error	32			
DGT				
Treatment	6	37.1689	2.32	0.064
Soil	1	17.2265	30.06	0.000
Treatment x Soil (1&2)	3	0.08973	0.22	0.723
Error	35			