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Author(s)	Shi, W.; Fenton, Owen; Ashekuzzaman, S. M.; Daly, K.; Leahy, J. J.; Khalaf, N.; Chojnacka, K.; Numviyimana, C.; Warcho, J.; Healy, Mark G.
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Phosphorus fertiliser equivalent value of dairy processing sludge-derived STRUBIAS products using ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum*)

W. Shi[1,2], O. Fenton[1,2] *, S.M. Ashekuzzaman[3], K. Daly[1], J.J. Leahy[4], N. Khalaf[4], K. Chojnacka[5], C. Numviyimana[5], J. Warchoł[5], M.G. Healy[2]

[1]Environment Research Centre, Teagasc, Johnstown Castle, Wexford, Co. Wexford, Ireland

[2]Civil Engineering and Ryan Institute, College of Science and Engineering, University of Galway, Ireland

[3]Department of Civil, Structural and Environmental Engineering, and Sustainable Infrastructure Research & Innovation Group, Munster Technological University, Cork, Ireland

[4]Chemical and Environmental Science, University of Limerick, Limerick, Ireland

[5]Department of Advanced Material Technology, Faculty of Chemistry, Wroclaw University of Science and Technology, ul. M. Smoluchowskiego 25, Wroclaw 50-372, Poland

Corresponding author: owen.fenton@teagasc.ie

Highlights

- STRUBIAS products derived from dairy sludge were tested for agronomic performance.
- Not all of the products tested showed good agronomic performance.
- High Fe content limits the fertiliser value of struvite and hydrochars.
- Generic guidelines based on a particular group of bio-based fertilisers are flawed.
- Removal of Fe from STRUBIAS products will improve agronomic performance.

Abstract

Struvite, biochar and ash products (collectively known as STRUBIAS) derived from different waste streams are used as fertilisers in agriculture. Raw dairy processing sludge (DPS) shows promise as bio-based fertilisers, but their secondary STRUBIAS-derived products need testing as fertilisers. The objective of this ryegrass (*Lolium perenne L.*) and wheat (*Triticum aestivum*) pot trial was to calculate their phosphorus mineral fertiliser equivalency (P-MFE) using the apparent P recovery (APR) method for Fe-DPS and DPS-derived struvites (Struvite 1 – 4), hydrochars (HC1 – 3) and ash. Results showed that the products can be divided into two groups: (1) a range of products that can (i.e., Struvite 1 – 3) and (2) cannot (i.e., Struvite 4, HC1 – 3, ash and Fe-DPS) be considered as fertilisers. In the first group, the P-MFE ranged from 66.8 to 76.7% for ryegrass and from 77.9 to 93.5% for spring wheat grain. In the second group, the P-MFE ranged from 7.8 to 58.3% for ryegrass and from -34.5 to -151.3% for spring wheat grain. The negative agronomic effects of some products for wheat grain (struvite and HC) in this study were mainly caused by high Fe content which could be overcome by improved treatment processes. Future policy and research must be aware that not all STRUBIAS products are suitable as fertilisers and therefore need to be tested individually.

Keywords: dairy processing; bio-based fertilisers; phosphorus mineral fertiliser equivalence value; STRUBIAS.

1. Introduction

In the European Union (EU) the dairy industry is the largest industrial food wastewater contributor (Shi et al., 2021). This waste is phosphorus (P)-rich and leads to large volumes of solid organic waste, referred to as dairy processing sludge (DPS). There are several types of DPS, with altered chemical characteristics based on the chemicals (i.e. salts containing Al, Fe, or Ca, etc.) used to treat waste, all of which have different nutrient and metal concentratiions and mineral fertiliser equivalence value (MFE) (Ashekuzzaman et al., 2019; Shi et al., 2022). Similar to other organic fertilisers, land application of DPS occurs only at certain times of the year (Sommer and Knudsen, 2021). This results in storage requirements and may result in nitrogen (N) losses through gaseous emissions. Therefore, technologies that process raw DPS on site are cost-efficient ways to recover nutrients from waste. Conversion of DPS (with the addition of other feedstock) into struvite, biochar (char-based materials) or ash (collectively called STRUBIAS) before land application is one such technology (Hu et al., 2022; Shi et al., 2021). STRUBIAS materials are recognised as fertilisers in the EU (EC, 2019; Huygens et al., 2018) and are expected to be certified to trade on the EU fertiliser market by 2030 (Huygens et al., 2018). DPS-derived STRUBIAS products are a new subset of products which, to date, have only been characterised in terms of their nutrient and metal concentrations (Shi et al., 2021), while its agronomic performance has rarely been reported (Shi et al., 2022).

The characterisation and agronomic performance of different STRUBIAS products varies considerably. Struvite (magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$)) is a mineral of P formed at treatment plants during the anaerobic digestion process whereby the pH and Mg levels are increased (Hertzberger et al., 2020). Struvite is considered to be a good slow-release fertiliser, as it normally has similar fertiliser efficiency to common mineral P fertilisers such as super phosphate (SP) and triple superphosphate (Johnston and Richards, 2003). However, the chemical composition of waste-recovered struvite is not consistent with pure struvite (Hall et al., 2020), leading to a variation in fertiliser performance. In addition, Al, Ca, Fe, and other toxic heavy metals can also precipitate along with struvite and affect the fertiliser efficacy (Li et al., 2019). Biochar is made from the thermochemical conversion of biomass in an oxygen-depleted atmosphere (Atallah et al., 2020) with different thermochemical pre-treatment processes, conditions and feedstocks, resulting in different products (Amoah-Antwi et al., 2020). Hydrothermal carbonisation (HTC) is a wet thermochemical process at the temperature range of 180-260 °C (Kambo and Dutta, 2015) and produces hydrochar. During this process an additional liquor is produced containing small-chain organic acids, ammonium (NH_4) and phosphate (Becker et al., 2019). Ash is produced from the incineration of bio-based materials by oxidation (Huygens et al., 2018) and contains K, P, S, Ca and Mg (Brod et al., 2012; Haraldsen et al., 2011; Knapp and Insam, 2011) and levels of P that are comparable to chemical equivalents (5.98% - 11.2% total P; Xu et al., 2012).

The objective of this study is to examine the phosphorus mineral fertiliser equivalent value (P-MFE) of a range of DPS-derived STRUBIAS products, since they are mainly P recovery products. We hypothesised that DPS could be a potential feedstock for STRUBIAS material and will show different agronomic performance depending on their characterisation. Suggestions of processing solutions will be provided when there is a shortfall in agronomic performance of the STRUBIAS materials. The results can give guidance to the fertiliser and agricultural industries with respect to these new emerging bio-based fertilisers and their efficacy.

2. Materials and methods

2.1 Sample collection, preparation and analysis

In this study four types of struvite (hereafter referred to as Struvite 1, 2, 3, and 4), one type of ash, Fe-DPS, three types of hydrochar (hereafter referred to as HC1, 2, and 3), and one reference mineral P fertiliser (SP) were used. The production process is illustrated in Figure 1. Struvite 1, 2 and 3 were precipitated from cheese production wastewater by varying the Ca:P, Mg:P and pH

(Numviyimana et al., 2020), and Struvite 4 was precipitated from HTC liquor (Numviyimana et al., 2022). Ash was created using a biochar (Kwapinska et al., 2019) processed in a laboratory furnace at 650 °C for 3 hours, cooled to room temperature, and then ground using a pestle and mortar. HC1, 2, and 3 were produced using a HTC process using Fe-DPS with different moisture contents. There was no additional water added in the reactor liner during the HC1 process. One percent H_2SO_4 was added in the reactor vessel with the DPS sample (set at 200 °C) to achieve moisture contents of 85% (HC2) and 90% (HC3), respectively. The liquor from HC2 was the feedstock of Struvite 4. Once the temperature was reached, the stirrer was operated at 25 rpm (HC1) and 36 (HC2 and HC3) rpm for 2 hours. Fe-DPS was collected from a dairy processing wastewater treatment plant in Ireland.

All DPS-derived STRUBIAS samples (Struvite 1-4, HC1-3 and ash) were characterised to determine their nutrient, metal and carbon (C) contents using the methodology presented in Shi et al. (2022). Briefly, pH was determined using a Jenway 3510 pH meter. Nutrients and metals were examined by an Agilent 5100 synchronous vertical dual view inductively coupled plasma optical emission spectrometer (Agilent 5100 ICP-OES) following the microwave-assisted acid digestion of samples. A high temperature combustion method (LECO TruSpec CN analyser) was used to determine total carbon (TC) and total nitrogen (TN). Mineral N was analysed colorimetrically following with 0.1M HCl extraction using an Aquakem 600 Discrete Analyser.

2.2 Pot design for P-MFE of STRUBIAS products

Soil samples were collected at Teagasc, Johnstown Castle Environmental Research Centre (52° 17′N, 6° 29′W) in Ireland and physically and chemically characterised for dry bulk density, water holding capacity (WHC), moisture content, soil mineral N, soil pH, organic matter (OM), total concentrations of nutrients and metals, and Morgan’s P using the methodology presented in Shi et al. (2022) and the results are shown in Table 1. Briefly, bulk density and WHC were measured using the method of Wilke (2005). The moisture content was determined using BS 1377-1 (BSI, 2016). Soil mineral N was analysed colorimetrically after extraction by 1M KCl. Soil OM was measured by loss on ignition using BS 1377-3 (BSI, 1990). Soil pH, total concentrations of nutrients and metals was measured using the same methodology as for STRUBIAS samples. Plant available P was measured with Morgan's P extracting solution (Morgan, 1941). The result of soil Morgan's P indicated that the soil was P deficient (< 3.0 mg L^{-1}) (Teagasc, 2020). The soil used in the pot trial was air dried for a week before sieving to <4 mm. Pot trials, comprising two crops, ryegrass (*Lolium perenne L.*) and wheat (*Triticum aestivum*), were set up to examine the P-MFE following the methodology of Sigurnjak et al. (2017), whereby two litre-capacity pots were filled as follows: a 2 cm-deep layer of gravel was added to the pots followed by 0.5 kg of soil and the remaining soil (1.3 kg) was mixed with the respective DPS-derived STRUBIAS materials and then added. Each layer of soil was compacted using a circular disk to a target dry bulk density of 1.2 g cm^{-3}. Finally, distilled water was added to reach a 70% WHC target.

The results of a previous study conducted by Shi et al. (2022) indicated that an application rate equivalent to 40 kg P ha^{-1} for ryegrass and 50 kg P ha^{-1} for spring wheat was optimal for plant growth. All the application rates were transformed to the pot experiment depending on taking the surface area of the pot into account. The final P rate was 91 mg P pot^{-1} for ryegrass and 113 mg P pot^{-1} for spring wheat. Therefore, these rates were used in the current study. STRUBIAS treatments (i.e., Struvite 1 – 4, with Struvite 4 only applied on spring wheat due to experimental logistical issues), ash, HC1-3, raw Fe-DPS, and SP were applied at one application rate for each crop. A study control (without P fertiliser) for each crop was also included in the experiments. Mineral fertilisers (i.e., calcium ammonium nitrate (CAN), potassium chloride (MOP) and sulphate of potash (SOP)) were applied to all pots to ensure that P was the only limiting nutrient (Table S1 and S2). Mg fertiliser was not added since extra Mg fertiliser is only advisable if soil Mg is less than about 50mg/l, while the Morgan's Mg of the soil used was 177 mg/l (Teagasc, 2020). Every treatment had three replications.

For ryegrass pots, 0.6 g of seeds (equivalent to 28 g m^{-2}) were seeded per pot. For wheat, 10 germinated wheat seeds were seeded in each pot (Darch et al., 2019). The pots were placed in a randomised block layout within a controlled growth chamber (Teagasc, Johnstown Castle) and operated under the following conditions: (1) 16-hour light photoperiod (2) daytime temperatures of 14 °C and night-time temperatures of 8 °C, with respective relative humidities of 85% and 75%, and (3) photosynthetically active radiation of 450 ± 50 μmol m^{-2} s^{-1}. All pots were held between 70 and 80% WHC by regularly weighting them. The grass was manually cut 4 cm above soil level after reaching a length of 22 – 26 cm. The grass pot trial lasted 16 weeks and 3 cuts were taken. The wheat plants were grown to maturity (20 weeks) and then separated into grain and chaff + straw after harvesting (Darch et al., 2019).

2.3 Crop and soil sampling and analysis

Fresh harvested crop samples were oven-dried at 70 °C for 72 hours in perforated plastic bags. Once dried, dry weight was recorded for dry matter (DM) analysis and, subsequently, dried samples were grounded and sieved to < 2 mm for nutrient and metal analysis. Soil samples before and after the pot trial were oven-dried at 40 °C for 72 hours and then sieved to <2 mm and analysed for nutrients and metals as for the field soil (Table 1).

2.4 P-MFE and statistical analysis

Shi et al. (2022) examined different methods to determine the agronomic performance of DPS. As a result of that study, the P-MFE (equation 2) calculated from apparent P recovery (APR) (equation 1) was deemed most suitable to present agronomic performance of P and is used in the current study.

$$APR(\%) = \frac{P\ uptake_{Treatment} - P\ uptake_{Control}}{Total\ P\ applied_{Treatment}} \qquad (1)$$

where APR is the difference in P uptake between treatment (P uptake$_{\text{Treatment}}$) and unfertilised pots (P uptake$_{\text{Control}}$) (Murphy et al., 2013).

$$\text{P-MFE}\ (\%) = \frac{APR_{Treatment}}{APR_{Reference}} \times 100 \qquad (2)$$

where P-MFE is the ratio between the apparent nutrient recovery of organic residues ($APR_{\text{Treatment}}$) and the mineral fertiliser applied at the same rate (‘reference’) (Sigurnjak et al., 2019).

Statistical analysis was performed using SAS statistical software (SAS, Statistical Analysis System, 2013). One-way analysis of variance (ANOVA) was performed for every dataset of crop yield and crop P uptake to determine if differences were seen as a function of treatment. Statistically significant differences were considered at a p-value ≤ 0.05 and where significance was found, a Fisher’s Least Significant Difference (LSD) test was used to determine statistical differences in means as a function of treatment for each variable at each harvest.

3. Results

3.1 Characterisation of nutrients and metals

The DPS-derived STRUBIAS products differed in their nutrient and heavy metal contents (Table 2). Comparing with the minimum nutrients requirements in the EU fertiliser regulation i.e. (1% by mass of TN and 1% by mass of P_2O_5 for solid organic fertiliser; 2% by mass of TN and 2% by mass of P_2O_5 for solid organo-mineral fertiliser) (EC, 2019), all products had high P contents and therefore met the minimum P requirement. However, the TC content of struvite 4 and ash was too low and therefore these products cannot be considered as organic fertilisers under the EU fertiliser regulation. The characterisation results suggested that all products had potential as fertilisers from at least a nutritional perspective. The heavy metal content of the ash was much higher than that of the other products. However, all products had heavy metal content below EU regulated limits (Cu, Ni, Pb, Cd, Zn, Hg and As) (EU, 2019).

3.2 Crop yield and P uptake

In the ryegrass study, cumulative yields and P uptake of DPS or STRUBIAS treatments were significantly higher than those of the control (no P treatment), except for Struvite 4 and ash (Table 3). The lowest ryegrass yields were measured in these two treatments, while high yields were achieved with Struvite 1 and 3, and HC1 and 3, which also had a similar yield to mineral P fertiliser. For P uptake, only Struvite 1 – 3 and HC1 treatments were significantly higher than the control and for Struvite 2 and 3, P uptake was in the same order of magnitude as for SP. In the spring wheat study, there was no significant difference between chuff + straw and grain yields of the control and all treatments, except ash for chuff (Table 3). This result indicated that the recommended P application rates might still not be enough to increase plant-available P in deficient soils (Croffie et al., 2020). Therefore, higher P concentrations should be applied in future studies to achieve a higher crop yield response and P uptake result. The lowest grain yield was found in the ash treatments, with the highest grain yield achieved with Struvite 1 and 2. All treatments had similar yields to mineral P fertiliser.

3.3 P-MFE for ryegrass and spring wheat

The APR and the corresponding P-MFE results of the ryegrass and spring wheat studies are presented in Table 4. The highest APR was observed for SP treatment in both ryegrass and spring wheat pot trial, which demonstrated that mineral P fertiliser is more readily available for plant uptake. The P-MFE of the DPS-derived STRUBIAS materials ranged from 7.8 to 76.7% for ryegrass and from -151.3 to 93.5% for spring wheat grain. Struvite 1-3 treatments had the highest P-MFE (66.8-76.7% for ryegrass and 77.9-93.5% for spring wheat grain), while ash had the lowest among all types of STRUBIAS materials examined in this study. Negative P-MFE results were found in ash, HC and Fe-DPS treatments in the spring wheat grain trial.

4. Discussion

4.1 Variation in chemical characteristics

The chemical characteristics of all STRUBIAS products are different and are mainly caused by the feedstock and treatment process, so generic fertiliser guidelines, based solely on the type of end products, are flawed. Struvite products had high concentrations of P and Mg, with metal concentrations lower than legal limits (EU, 2019). Struvites 1 - 3 were generated from cheese production wastewater (whey) with different pH and salt dosages, resulting in different nutrient concentrations (Numviyimana et al., 2020). Struvite 1 was produced under optimal conditions (highest struvite content) and contained the highest amounts of nutrients, while Struvite 3, produced with a high dose of calcium salts, had low nutrient but a high Ca content. The P recovery of Struvite 3 was improved by chemical precipitation with Ca. However, this resulted in lower fertiliser quality as the Ca addition caused the loss of ammonium and P availability. Struvite 4 was precipitated from the HC2 liquor and contained high amounts of Fe due to the feedstock used. Both Ca and Fe are known to negatively affect the availability of P in soil (Ashekuzzaman et al., 2021). All ash and HC samples contained a significant amount of nutrients and metals, except NH_4-H, because P and metals are most likely to remain and concentrate in solid residues during thermo-chemical process (Shackley et al., 2010). Three HCs in this study were produced from a Fe-DPS and different initial acidity was used, which can affect HC yield (Khalaf et al., 2022) but did not affect the HC characteristics.

4.2 Problems and solutions for the tested STRUBIAS products

The results of this study suggest that not all STRUBIAS products of dairy waste are suitable as fertilisers. For example, struvite is normally considered to be an excellent fertiliser, because it has similar fertiliser efficiency to common mineral P fertilisers (Johnston and Richards, 2003). However, in this study, only three of the four struvites tested showed good potential as fertilisers. Struvite 4, precipitated from HC2 liquor, produced a low ryegrass yield and consequently had a low P-MFE. Numviyimana et al. (2020) conducted a citric acid nutrient release assay on Struvite 3 (the same product as used in the current study) and their results showed lower nutrient availability (P, Mg, NH_4^+) in that product, which was also observed in the current study. Furthermore, Numviyimana et al. (2020) also found that Struvite 1 had slow P release properties, which may explain the higher grass yields and P uptake in the last ryegrass harvest in the current study (Table 3). The results of the literature show that struvite derived from different feedstocks exhibits a range of agronomic performance (Table S3). Szymańska et al. (2020) conducted a long-term pot experiment with struvite derived from cattle slurry. Higher P-MFE (~150% in silty loamy soils and ~140% in loamy sandy soils) was obtained in the second year of the experiment, with overall results outperforming commercial ammonium phosphate. The results indicated that struvite was an excellent slow-release P fertiliser and might have better agronomic performance than mineral P fertilisers in the long term. González-Ponce et al. (2021) conducted a 90-day pot experiment with struvite derived from anaerobically digested sewage sludge on grass. Increased APRs (~10%) were obtained from these samples and the highest APRs (11.5 ± 3.8 and 15.7 ± 5.5) were obtained from treatments with struvite of a larger particle size. All these results suggested that the plants efficiently used the P contained in the struvite.

The high Fe content of Struvite 4 resulted in its poor agronomic performance. Iron exhibits a high precipitation potential for struvite but limited fertiliser quality of struvite (Numviyimana et al., 2022). This is due to the lower water solubility (K_{sp}) of iron salts such as vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$, $K_{sp} = 10^{-35.8}$) than struvite ($K_{sp} = 10^{-13.17}$) (Hanhoun et al., 2011; Priambodo et al., 2017). Numviyimana et al. (2022) conducted cucumber growth experiments using Struvite 4 and observed very low germination rates (32%), which was attributed to phytotoxicity issues associated with metals. However, the fertiliser quality of Struvite 4 could be improved if Fe was removed during the processing chain: Numviyimana et al. (2022) used oxalic acid for better struvite precipitation, which removed Fe from the process chain, resulting in much higher cucumber germination rates (88%). Therefore, struvite from waste streams should not be assumed to be a good fertiliser without testing, and, where needed, processing modifications can be implemented to overcome shortfalls in its agronomic performance.

Although the ash had a high P content, it produced the lowest crop yield (and therefore P-MFE) in both the ryegrass and spring wheat trials. Compared to the study control, ash inhibited the growth of spring wheat. The negative P-MFE in the spring wheat trial also implied a slow P release and a low P uptake. This was because P in ash normally occurs as Fe, K, and Ca phosphate (Tan and Lagerkvist, 2011), and therefore the solubility of P is likely to be low. In some cases, ash has been reported to increase the yield or P-MFE of agricultural crops (Battisti et al., 2022; Kuligowski et al., 2010), while other studies reported that ash did not significantly affect or even inhibited, plant growth (Kominko et al., 2019; Ochecova et al., 2014) (Table S3). These varying results may be attributed to the difference in the type of feedstock or the post-treatment process, which affects the solubility of P (Møller et al., 2007; Rubæk et al., 2006). For example, acidification can transform P in ash into a more soluble form. Kuligowski et al. (2010) found that using sulfuric acid as an extractant and potassium hydroxide as a neutraliser is capable of making ash P highly available. Buneviciene et al. (2020) found that granulated biofuel ash significantly increased spring barley grain and straw yields compared to ash powder.

Positive and negative agronomical effects were observed for HC treatments, with HC 1 – 3 performing significantly better in ryegrass when compared to the spring wheat study. The HTC process improved the agronomic value (yield and P-MFE) compared to its feedstock (Fe-DPS), and the different initial acidities did not affect its agronomical performance. The experiments indicated that HC can be (depending on its individual properties) a good fertiliser for ryegrass, but the negative P-MFE for spring wheat implied a slow release of P and low crop P uptake compared to the control of the study. The fertiliser potential of HC is very complex and depends on many variables, such as the type of soil, type of crop, application rates, HTC process conditions, feedstock, time in the soil, and experimental conditions (field/pot) (Melo et al., 2018). Many studies have observed different agronomic performances of HC (Table S3). For example, Melo et al. (2018) reported a positive Phaseolus bean yield response after application of sewage sludge derived HC with soil fertility and soil quality benefits. Furthermore, a longer residence time of HC in the soil enabled better nutrient uptake by the crop due to the slow release of nutrients. Gajić and Koch. (2012) applied HC derived from sugar beet pulp and beer draff in the field with different mineral N fertiliser treatments and found that HC, especially with its high C/N ratio, inhibited sugar beet growth due to its high N immobilizing potential. Xia et al. (2020) found that HC derived from pinewood sawdust inhibited the growth of paddy rice in both root and stem. On the contrary, Xia et al. (2020) observed a significant positive effect on rice treated with aminofunctionalised hydrochar (by polyethylenimine grafting) and this HC product effectively reduced heavy metal uptake by the plant. Therefore, although HC derived from DPS has potential as a fertiliser, more research is still needed to identify suitable feedstocks, possible risks, inhibiting mechanisms and substances, and technologies to reduce risks or improve nutrient availability.

Currently and more increasingly into the future, farmers and growers will be encouraged to use less mineral fertiliser and to choose bio-based alternatives. As bio-based fertilisers are heterogeneous in nature (differential origin and processing lead to heterogeneous characteristics), a standardised procedure to examine the agronomic performance of each bio-based fertiliser alternative must be applied. As each new bio-based product emerges, the following chain is suggested: (1) documentation of how the product was processed, (2) total and available nutrient and metal concentration must be conducted using standard methods, and (3) elucidation of its N and P-MFE stating in detail the methodology and calculation methods used. Step 3 must be transparent and well documented, as N and P-MFE values differ depending on the methods used, and (4) this process needs to be repeated for each type of bio-based fertiliser and crop combination. Without this thorough chain of investigation in place, assumptions regarding a particular group of bio-based fertilisers may be too generalised. For example, in the current study, not all products defined as struvite were considered potential fertilisers.

5. Conclusions

In this study, the agronomic performance of different DPS-derived STRUBIAS materials was determined, but not all the materials tested were deemed suitable as fertilisers to be used in agriculture. Only three of the four struvites tested showed good agronomic performance. The fertiliser value of the fourth struvite and the hydrochars was limited by their high Fe content, which could be overcome by exclusion of the use of iron salts in the removal of P to comply with discharge licence requirements in processing plants. Ash treatments exhibited very low or even negative P-MFEs. These results indicate the importance of testing every bio-based fertiliser alternative to determine their agronomic performance, before making a decision regarding their suitability as fertilisers to be used in agricultural crops. In addition, such testing can guide the processing of STRUBIAS products where low or even negative P-MFEs are determined. Future policy and research must be aware that not all STRUBIAS products will be suitable as fertilisers. Therefore, STRUBIAS products derived from different wastes will continuously need to be evaluated to examine their nutrient and metal concentrations, along with their agronomic performance as fertilisers.

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Table 1. Characteristics of the soil used in the pot trial.

Clay %	Silt %	Fine Sand %	Coarse Sand %	Organic Matter %	Total N mg/kg	Total P mg/kg	Total K mg/kg	Total Al mg/kg	Total Ca mg/kg	Total Fe mg/kg	Morgan’s P mg/l	pH
15.0	30.1	34.6	20.3	6.5	2700	582	2640	14191	1367	13143	1.9	5.8

Table 2. Characterisation of dairy processing sludge derived STRUBIAS products

Parameters	Struvite1	Struvite2	Struvite3	Struvite4	Ash	HC1	HC2	HC3	Fe-DPS	Min.	Max.	Mean ± SD
pH	7.9	8.3	8.8	9.0	9.3	6.9	7.9	7.7	7.6	6.9	9.3	8.2 ± 0.72
TN (g kg^{-1})	43.7	29.4	11.2	4.99	1.1	37.5	29.4	36.5	68.3	1.1	68.3	29.1 ± 19.9
NH_4-H (g kg^{-1})	40.4	15.4	0.33	1.1	0.092	0.0026	0.0031	0.0025	0.35	0.0025	40.4	6.4 ± 12.9
TP (g kg^{-1})	104.2	80.2	47.0	59.0	99.3	78.9	85.4	79.9	57.2	47.0	104.2	76.8 ± 18.1
TC (%)	10.7	25.9	38.8	0.20	0.90	22.6	18.4	21.2	32.7	0.20	38.8	21.4 ± 12.6
K (g kg^{-1})	7.1	7.5	6.5	7.0	26.7	13.5	8.5	12.6	15.3	6.5	26.7	11.6 ± 6.1
Mg (g kg^{-1})	101.3	62.2	18.8	72.8	17.0	3.7	3.7	3.5	2.9	2.9	101.3	31.8 ±35.0
S (g kg^{-1})	0.16	0.46	0.62	0.07	11.9	3.2	12.8	8.2	4.3	0.07	12.8	4.6 ± 4.8
Na (g kg^{-1})	2.6	8.8	31.7	65.2	20.5	2.8	1.8	2.6	3.0	1.8	65.2	15.4 ± 20.1
Ca (g kg^{-1})	14.7	34.5	66.9	21.2	227.5	68.0	72.0	65.7	49.2	14.7	227.5	68.9 ± 59.6
Cr (mg kg^{-1})	2.2	2.8	3.3	2.6	41.2	6.5	6.8	6.8	5.3	2.2	41.2	8.6 ± 11.7
Cu (mg kg^{-1})	1.8	0.21	0.38	0.82	92.7	47.8	6.1	5.4	4.2	0.21	92.7	17.7 ± 30.1
Ni (mg kg^{-1})	<0.6	<0.6	<0.6	<0.6	27.4	7.6	9.4	9.1	7.0	<0.6	27.4	6.8 ± 8.3
Pb (mg kg^{-1})	<2	<2	<2	<2	32.6	5.9	5.9	5.3	4.3	<2	32.6	6.1 ± 9.7
Zn (mg kg^{-1})	30.1	34.4	36.2	6.9	482.4	186.1	185.9	171.7	136.0	6.9	482.4	141.1 ± 139.1
Al (g kg^{-1})	0.02	0	0	0.05	82.1	8.0	8.5	7.8	6.1	0	82.1	12.5 ± 24.9
Fe (g kg^{-1})	0.07	0.17	0.39	31.4	7.5	177.3	199.7	183.4	128.7	0.07	199.7	80.9 ± 84.0

Co (mg kg^{-1})	<0.3	<0.3	<0.3	<0.3	4.9	11.0	11.3	11.0	9.6	<0.3	11.3	5.4 ± 5.0
Mo (mg kg^{-1})	<0.5	<0.5	<0.5	<0.5	11.1	<0.5	<0.5	<0.5	<0.5	<0.5	11.1	1.2 ± 3.5
Mn (mg kg^{-1})	0.53	0.57	2.24	10.2	609.6	234.7	247.9	230.3	181.7	0.53	609.6	168.6 ± 188.1
Cd (mg kg^{-1})	<0.15	<0.15	<0.15	<0.15	0.68	<0.15	0.25	<0.15	<0.15	<0.15	0.68	<0.15
As (mg kg^{-1})	<1.5	<1.5	<1.5	<1.5	4.1	<1.5	<1.5	<1.5	<1.5	<1.5	4.1	<1.5
B (mg l)	2.0	2.7	3.0	7.4	74.0	3.1	2.0	2.4	1.7	1.7	74.0	10.9 ± 22.4
Se (mg kg^{-1})	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Abbreviations used in table: HC=hydrochar; DPS=dairy processing sludge; SD=Standard deviation; TN=total nitrogen; TP=total phosphorus; TC=total carbon.

Table 3. Effect of treatment and P rate on the grass and spring wheat dry matter yield and P uptake over the course of the P-MFE experiment.

Treatment*	P rate kg ha^{-1}	Yield (g)				P uptake (mg pot^{-1})			
		Ryegrass							
		1*	2*	3*	**cumulative**	1*	2*	3*	**cumulative**
Control	0	2.6^{d} (0.8)	2.0^{f} (0.5)	1.9^{f} (0.3)	**6.5^{f} (1.0)**	728^{d} (250)	605^{c} (146)	390^{f} (43)	**1723^{d} (190)**
SP	40	5.1^{bc} (1.8)	5.3^{a} (1.5)	8.8^{a} (1.5)	**19.2^{a} (2.9)**	1982^{a} (685)	1331^{a} (400)	1168^{a} (156)	**4482^{a} (857)**
Struvite1	40	5.7^{bc} (0.8)	4.4^{abc} (1.1)	7.6^{bcd} (0.1)	**17.7^{ab} (2.2)**	1282^{bc} (292)	1230^{ab} (430)	1054^{ab} (30)	**3565^{bc} (219)**
Struvite2	40	8.3^{a} (1.9)	3.7^{bcde} (0.2)	3.3^{ef} (0.9)	**15.2^{bc} (2.4)**	1922^{a} (205)	1100^{abc} (204)	646de (112)	**3667^{ab} (269)**
Struvite3	40	7.4^{a} (0.8)	4.7^{ab} (0.4)	4.0^{de} (0.4)	**16.1^{ab} (1.6)**	1875 ^{ab}(211)	1117^{abc} (218)	846^{ef} (149)	**3838^{ab} (252)**
Struvite4	40	3.0^{cd} (0.5)	2.7^{def} (0.3)	1.4^{f} (0.8)	**7.0^{f} (0.5)**	1166^{cd} (282)	821^{abc} (167)	412^{ef} (134)	**2399^{d} (186)**
Ash	40	3.5^{cd} (0.5)	2.8^{def} (0.4)	3.0^{ef} (0.1)	**8.3^{ef} (2.1)**	891^{cd} (208)	812^{bc} (101)	235^{f} (32)	**1938^{d} (193)**
HC1	40	4.8^{bcd} (1.0)	4.9^{ab} (0.6)	7.4^{abc} (1.4)	**17.1^{ab} (1.0)**	1169^{cd} (210)	1179^{ab} (236)	983^{abc} (95)	**3332^{bc} (350)**
HC2	40	3.5^{cd} (0.1)	3.3^{cdef} (0.3)	6.3^{bcd} (0.7)	**12.5^{bc} (0.3)**	992^{cd} (266)	947^{abc} (78)	737^{cd} (109)	**2536^{cd} (532)**
HC3	40	4.0^{bcd} (1.2)	4.3^{abc} (0.5)	7.8^{ab} (1.0)	**16.1^{ab} (1.6)**	992^{cd} (329)	969^{abc} (281)	849^{bc} (23)	**2856^{cd} (460)**
Fe-DPS	40	4.0^{bcd} (1.0)	3.8^{bcde} (0.7)	4.3^{de} (0.4)	**12.1^{cd} (1.3)**	1084^{cd} (236)	920^{abc} (254)	453^{ef} (144)	**2457^{d} (283)**
		Spring wheat							

		Chuff + Straw	Grain	Chuff + Straw	Grain
Control	0	19.2^{ab} (2.0)	13.6^{ab} (2.4)	522^{ab} (100)	2995^{ab} (135)
SP	50	17.6^{ab} (4.8)	10.9^{ab} (1.6)	816^{a} (632)	4016^{a} (946)
Struvite 1	50	20.8^{a} (2.3)	14.4^{a} (1.4)	703^{ab} (85)	3879^{a} (252)
Struvite2	50	20.6^{a} (3.5)	14.5^{a} (5.4)	1089^{a} (534)	3948^{a} (927)
Struvite3	50	19.5^{a} (2.5)	11.7^{ab} (3.3)	983^{ab} (515)	3766^{a} (490)
Ash	50	11.9^{c} (3.6)	6.7^{b} (1.0)	272^{b} (67)	1225^{d} (215)
HC1	50	18.8^{ab} (2.8)	10.9^{ab} (3.2)	386^{ab} (124)	2496^{bcd} (283)
HC2	50	17.0^{abc} (3.1)	11.1^{ab} (4.6)	476^{ab} (282)	2518^{bc} (705)
HC3	50	16.4^{abc} (0.2)	11.8^{ab} (2.5)	408^{ab} (52)	2314^{bcd} (712)
Fe-DPS	50	14.2^{bc} (3.3)	8.0^{b} (2.8)	749^{ab} (432)	1724^{cd} (624)

Mean comparison by Fisher's Least Significant Difference (LSD) test ($p \leq 0.05$); Within columns shared letters denote no difference ($p > 0.05$), and unshared letters denote a statistical difference ($p \leq 0.05$); Values indicated in brackets are standard deviations ($n = 3$). Abbreviations used in table: SP=super phosphate; HC=hydrochar; DPS=dairy processing sludge.

[*] Three cuts of ryegrass.

Table 4. Ryegrass and wheat grain pot trial results for dairy processing sludge and derived STRUBIAS, rate applied in pot trial and % of mineral fertiliser equivalent value.

	P rate **kg ha^{-1}**	**APR from Eqn. 1** **%**	**P-MFE from Eqn. 2** **%**
		Ryegrass	
SP	40	30.4	100.0
Struvite 1	40	20.3	66.8
Struvite 2	40	21.4	70.5
Struvite 3	40	23.3	76.7
Struvite 4[1]	40	7.5	24.5
Ash	40	2.4	7.8
HC1	40	17.7	58.3
HC2	40	10.7	35.1
HC3	40	12.5	41.1
Fe-DPS	40	8.1	26.6
		Wheat grain	
SP	50	9.0	100.0
Struvite1	50	7.8	87.0

Struvite2	50	8.4	93.5
Struvite3	50	6.8	77.9
Ash	50	-15.6	-151.3
HC1	50	-4.4	-35.8
HC2	50	-4.2	-34.5
HC3	50	-6.0	-50.2
Fe-DPS	50	-11.2	-106.4

[1] Struvite 4 was not used in the spring wheat trial.

Abbreviations used in table: APR=apparent phosphorus recovery; P-MFE=phosphorus mineral fertiliser equivalent value; HC=hydrochar; DPS=dairy processing sludge