Research article

Mineral fertiliser equivalent value of dairy processing sludge and derived biochar using ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum*)

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ABSTRACT

As supply chains of chemical fertilisers become more precarious, raw or derived bio-based fertilisers (herein referred to as bio-fertilisers) from the dairy processing industry could be good alternatives. However, their agronomic performance is relatively unknown, and where documented, the method to estimate this value is rarely presented. This pot study investigated aluminium-precipitated and calcium-precipitated dairy processing sludges (Al and Ca-DPS) and DPS-derived biochar as potential bio-fertilisers to grow ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum*). The study aims were to examine how (1) application rate (optimal versus high) and (2) calculation methods (with and without chemical fertiliser response curves) can affect estimates of nitrogen and phosphorus mineral fertiliser equivalence value (N- and P-MFE) and associated agronomic advice. The results from both crops showed that for nitrogen application rates (125 or 160 kg ha^{-1} for ryegrass and 160 or 240 kg ha^{-1} for spring wheat) estimates of N-MFE increased for both Al-DPS and Ca-DPS as application rate increased. Dry matter yield response curves produced the highest % N-MFE results (e.g., ryegrass ~50% and 70% for Al-DPS and Ca-DPS) with other calculation methods producing all similar results (e.g., ryegrass ~20% for Al-DPS and Ca-DPS). For phosphorus application rates (40 or 80 kg ha^{-1} for ryegrass and 50 or 80 kg ha^{-1} for spring wheat), estimates of P-MFE did not increase with application rate. Negative P-MFE values obtained for Ca-DPS and DPS-biochar when growing ryegrass and spring wheat grain, respectively, indicated low plant available phosphorus. Overall, Al-DPS had better performance as a bio-fertiliser when compared to the other products tested. There was no significant difference between the two calculation methods of MFE, which suggests that the determination of MFE could be simplified by using one application as opposed to numerous application rates of fertilisers. Future work should focus on elucidating the N- and P-MFE of a wider range of DPS and STRUBIAS bio-fertilisers, and alternative methods should be investigated that enable a comparison across all bio-fertiliser types.

1. Introduction

The global and European bioeconomy face multiple challenges, one of which is to choose safe alternatives to chemical fertiliser that can grow crops (EC, 2019). This is particularly pertinent in recent times, as due to trade embargos between the European Union (EU) and Russia (from which a lot of fertiliser is imported into EU countries) (Lehikoinen et al., 2021) supply bottlenecks in agricultural inputs have occurred which have resulted in increased fertiliser prices. The milk processing industry may be an alternative fertiliser source, as wastewater treatment systems used in the dairy industry generate large volumes of solid or liquid wastes such as dairy processing sludge (DPS) (Hu et al., 2021).

In Europe, about 3.8 million tonnes of DPS (fresh weight) is generated annually, corresponding to about 155 million tonnes of EU milk production per year (Ashekuzzaman et al., 2021a). As chemical precipitation of phosphorus (P) using lime, iron (Fe) or aluminium (Al) is the main method for P removal in these systems, DPS may be categorised into three types: calcium-precipitated (Ca-DPS), iron-precipitated (Fe-DPS), and aluminium-precipitated (Al-DPS). Since all the DPS types have a high nutrient and low metal content (Ashekuzzaman et al.,

2019), the main disposal pathway is agricultural land spreading as a bio-based fertiliser (herein referred to as bio-fertiliser). Care must be taken in the land application of fertilisers so as to avoid P loss and environmental pollution (Peyton et al., 2016; O' Flynn et al., 2018). Nutrients, especially P, in raw DPS may also be recovered by chemical methods, such as precipitation or adsorption, and thermal-chemical methods. This results in the creation of fertilising products including struvite, biochar and incineration ashes, collectively referred to as STRUBIAS (Huygens et al., 2018).

The agronomic performance of bio-fertilisers is assessed using a range of different methodologies (e.g., glasshouse or controlled environment pot trials, field trials, P bioavailability using diffusive gradients in thin films, etc.). The methodology is rarely documented in the literature, making it difficult to compare agronomic performances of similar or different products (Kratz et al., 2019). A common method used is the mineral fertiliser (both P and N) equivalence value (P-MFE or N-MFE), which compares the performance of a candidate fertiliser to a reference fertiliser.

There are two methods used to assess MFE. The first method determines MFE by creating a response curve of crop yield or nutrient uptake by incremental additions of mineral fertiliser N or P (Delin, 2011; Lalor et al., 2011). A response curve is created by fitting a regression to the data (Fig. S1), where application rate is displayed on the x-axis and crop yield, or N or P uptake, is displayed on the y-axis. The MFE can be expressed as a percentage of total N or P applied in DPS (Eqns. (1) and (2)).

$$N - MFE \ (\%) \cdot = \cdot \frac{EQ_{mineral \ N \ fertiliser \ rate}}{N_{applied}} \times 100 \quad (1)$$

$$P - MFE \ (\%) \cdot = \cdot \frac{EQ_{mineral \ P \ fertiliser \ rate}}{P_{applied}} \times 100 \quad (2)$$

where $EQ_{mineral \ N \ or \ P \ fertiliser \ rate}$ is the equivalent amount of mineral N or P fertiliser that gives the same reference response compared to DPS, and $N_{applied}$ or $P_{applied}$ is the application rate of N or P in the DPS (Ashekuzzaman et al., 2021b). $EQ_{mineral \ N \ or \ P \ fertiliser \ rate}$ is determined using the regression between mineral fertiliser application rates (kg ha^{-1}) and crop response (N or P uptake or yield).

The second method assesses the MFE by calculating the apparent N or P recovery (ANR or APR) without using a response curve, which means that only one rate of mineral fertiliser N or P (the 'reference') is used instead creating a response curve using different application rates. The ANR and APR show the difference in N and P uptake between the treatment (N uptake$_{Treatment}$ or P uptake$_{Treatment}$) and unfertilised plots (N uptake$_{Control}$ or P uptake$_{Control}$) (Murphy et al., 2013) (Eqns. (3) and (4)). MFE is the ratio of the apparent nutrient recovery of organic residues (ANR$_{Treatment}$ or APR$_{Treatment}$) and that of mineral fertiliser applied at the same rate (Cavalli et al., 2016; Sigurnjak et al., 2019), and is determined using Eqns. (5) and (6).

$$ANR(\%) = \frac{N \ uptake_{Treatment} - N \ uptake_{Control}}{Total \ N \ applied_{Treatment}} \quad (3)$$

$$APR(\%) = \frac{P \ uptake_{Treatment} - P \ uptake_{Control}}{Total \ P \ applied_{Treatment}} \quad (4)$$

$$N - MFE \ (\%) \cdot = \cdot \frac{ANR_{Treatment}}{ANR_{Reference}} \times 100 \quad (5)$$

$$P - MFE \ (\%) \cdot = \cdot \frac{APR_{Treatment}}{APR_{Reference}} \times 100 \quad (6)$$

These methods apply conventional fertiliser response curves to bio-fertilisers. The response curves are derived from chemical fertiliser, which is 100% available (either N or P) and immediately soluble, with no other interfering elements. This is why it is important to state the method and the assumptions made when presenting MFE data.

The objective of this glasshouse pot trial was to examine how (1) application rate (optimal versus high) and (2) calculation methods (with and without response curve development) can affect N- and P-MFE estimates and associated agronomical performance. Currently, information on the N- and P-MFE of these products is scarce and this has resulted in low adoption of these products as fertilisers. The substitution of chemical fertiliser with bio-fertilisers could become increasingly important to achieve sustainable agricultural systems. The results presented are important as they comment on the agronomic performance of these products for the first time and also examine and contrast different calculation methodologies currently used in pot trials. The results of the present study must be considered when incorporating the MFE of bio-based fertilisers into nutrient management plans. Only where correct values are used can both yield and environmental outcomes be realised.

2. Materials and methods

2.1. DPS and DPS-derived biochar collection and characterisation

Two types of DPS (Al-DPS and Ca-DPS) were collected in plastic containers with sealed, vented lids from two dairy processing wastewater treatment plants in Ireland. They were stored at 4 °C before the start of the experiment. One biochar sample (i.e., DPS-derived biochar), produced from a mixture of dried biological sludge mixed with spruce wood chips at a ratio of 50:50 by weight and subsequently pyrolysed at a pilot-scale facility as recommended by Kwapinska et al. (2019), was also used in the experiment.

The dry matter (DM) and organic matter (OM) of DPS samples were determined using standard gravimetric method 2540G (APHA, 2005). The pH was determined in a 1:2.5 (w/v) ratio of fresh sludge to deionised water solution by a Jenway 3510 pH meter after 1 h mixing by an end-to-end shaker. The concentrations of nutrients (P, K, Mg, S, Na, Ca) and metals (As, Cd, Cr, Cu, Ni, Pb, Zn, Al, Fe, Co, Mo and Mn) were determined using 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 (Method 3050B, USEPA, 1996). The samples were analysed for total carbon (TC) and total nitrogen (TN) using a high temperature combustion method (LECO TruSpec CN analyser). The mineral fraction (total oxidized N and ammonium nitrogen (NH$_4$–N)) of total N was analysed colorimetrically in a 0.1M HCl-extracted filtered solution using an Aquakem 600 Discrete Analyser. For extraction, biochar and freeze-dried sludge powder samples were mixed with extracting solution (0.1M HCl) at a solid to liquid ratio of 1:20, shaken for 1 h, and then centrifuged at 3000 rpm for 5 min. Before analysis of mineral N, the supernatant was filtered using GF/A filter paper.

2.2. Soil collection and characterisation

Soil samples, to a depth of 0.1 m below the ground surface, were collected from a field site at the Teagasc, Johnstown Castle Environmental Research Centre (52° 17'N, 6° 29'W) in the southeast of Ireland. The soil was sandy loam (54.9% sand, 30.1% silt and 15.0 clay) and the plant available P, determined by Morgan's soil P extraction method (Teagasc, 2020), indicated that the soil was P deficient (<3.0 mg L^{-1}). The grass was removed, and the soil was mixed in large containers. Sub-samples of field-moist soil were taken for physicochemical determination. Bulk density and water holding capacity (WHC) was measured using the method of Wilke (2005). The moisture content was determined in accordance with BS 1377–1 (BSI, 1990). To determine soil mineral N (total oxidized nitrogen (TON), nitrite nitrogen (NO$_2$–N) and NH$_4$–N), field-moist soil was sieved to a particle size of <2 mm and extracted by shaking 20 g soil in 100 ml 1M KCl at room temperature for 1 h using an Aquakem 600 Discrete Analyser. The concentration of nitrate nitrogen (NO$_3$–N) was calculated by subtracting the concentration of NO$_2$–N from TON (Henriksen and Selmer-Olsen, 1970). Other soil samples were dried

in the oven at 40 °C for 72 h, after which they were sieved to <2 mm. Soil pH was then determined using a pH probe (Jenway 3510 pH meter) and a 2.5:1 ratio of deionised water-to-soil. Soil OM was determined by loss on ignition using B.S. 1377–3 (BSI, 1990). Total concentrations of P, Al, Fe, Ca and metals in soil were analysed using microwave-assisted acid digestion (USEPA, 1996). Total C and TN were measured by a high temperature combustion method (Wilke, 2005). Plant available P was measured with Morgan's P extracting solution (Morgan, 1941). The pipette method was used to determine the soil's sand-silt-clay % and determine the soil texture.

2.3. Pot experiment

The soil used in the pot trial is a light-textured clay loam with a low Morgan's P (Index 1 which is deficient in P) (Table 1). The soil to be used for both pot trials was then separated out on plastic sheets and air-dried for a week before sieving to <4 mm.

Two commonly used forage crops in Ireland were used: ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum*) (O' Donnell et al., 2021). Two litre-capacity pots of 0.13 m height with bottom and top diameters of 0.17 m and 0.15 m, respectively, were used (Fig. 1). For each pot, 1.8 kg of air-dried soil, sieved to a particle size of <2 mm, was added above a 2 cm-deep layer of gravel, which was used to improve drainage and avoid loss of soil. The pots were filled in two steps following a method described in Sigurnjak et al. (2017): 0.5 kg of soil was added to the pots and the remaining soil was mixed with the respective fertiliser materials and subsequently added to the pots. One day before the pot experiment commenced, distilled water was added to reach 70% WHC of the soil and each layer of soil was compacted by a circular disk to a bulk density of 1.2 g cm^{-3}, which was same as the field measured one.

Calcium ammonium nitrate (CAN) and super phosphate (SP) were used as the study reference (Eqns. (5) and (6)) in the N and P trials for each crop. The application rates of CAN and SP for ryegrass and spring wheat were based on the advised rates in Ireland (Teagasc, 2020) (Tables S1 and S2). Two DPS products were applied as N and P fertilisers at two rates. DPS-derived biochar was only used as P fertiliser, as the mineral N was low after high temperature combustion, and was also applied at two rates. Potassium chloride (MOP) and sulphate of potash (SOP) were applied to all pots as per recommended application rates for the study crops (Teagasc, 2020) to ensure that K and S were not limited. Then, depending on whether a N or P trial was being conducted, either SP or CAN were also added to ensure that either N or P was the only limiting nutrient (Tables S1 and S2). Every treatment had three replications. To avoid cross contamination between the experimental treatments, utensils were thoroughly cleaned and gloves were changed after different treatments. For the pots with perennial ryegrass, 0.6 g of seeds (equivalent to 28 g m^{-2}) were sown per pot. For wheat, 10 germinated wheat seeds were sown in each pot (Darch et al., 2019; González Jiménez et al., 2018). The pots were placed in a randomised block design in a glasshouse. Water was added to pots so that 70%–80% WHC was maintained. This was done by weighting them regularly and watering using tap water to attain the target WHC. The grass was cut manually to 4 cm above soil level once it reached a length of 22–26 cm. The wheat plants were harvested until maturity (20 weeks) and then separated into grain, and chaff + straw (Darch et al., 2019; González Jiménez et al., 2018).

2.3.1. Crop and soil sampling and analysis during the pot trial

All the fresh harvested plant samples were weighed and then oven-dried at 40 °C for 72 h in perforated plastic bags on the day of cutting (Darch et al., 2019). Once dried, dry weight was recorded for DM analysis and, subsequently, dried samples were grounded sieved to 2 mm size and used for nutrient analysis. Total crop P, K, S, Mg and Ca were all analysed using an Agilent 5100 synchronous vertical dual view inductively coupled plasma optical emission spectrometer (Agilent 5100 ICP-OES), following the microwave-assisted acid digestion of sieved samples (USEPA, 1996). Total N and carbon were analysed using a combustion analyser (LECO TruSpec CN analyser). Soil samples collected from each pot were oven-dried at 40 °C for 72 h and then sieved to <2 mm for chemical analysis.

2.3.2. Mineral fertiliser equivalence (MFE) of the bio-based products

All the data from the pot trials were used to develop a response curve of crop yield or nutrient uptake by incremental additions of mineral fertiliser N or P, and by assessing the MFE of the bio-based products by calculating the apparent N or P recovery (ANR or APR) without using a response curve. Statistical analysis was performed using SAS statistical software (SAS, Statistical Analysis System, 2013). Analysis of variance (ANOVA) was used to determine the effect of the different treatments and application rates on crop yield, crop P and N uptake.

3. Results & discussion

3.1. Characterisation of DPS and derived biochar

The physicochemical properties of two types of DPS and DPS-derived biochar used in the pot trial are shown in Table 2. The different types of DPS and DPS-derived biochar differed in their N and P contents. The Ca-DPS had a higher DM content and lower OM content than Al-DPS, reflecting the mixture with calcium oxide. The pH of the Al-DPS was near neutral (pH 7.7), while Ca-DPS had an alkaline pH of 12.4. The TN content in Al-DPS was much higher than Ca-DPS and biochar. The mineral N fraction in all DPS samples was predominantly NH$_4$–N. The NH$_4$–N concentration was very low in the Ca-DPS (1.2% of TN) and DPS-derived biochar (0.24% of TN), because lime addition and high temperature pyrolysis cause losses of NH$_3$ (Ashekuzzaman et al., 2019). This can also explain high C:N ratio of Ca-DPS (15.2) and biochar (14.6). Biochar had the highest TP concentration (52.3 g kg^{-1}) on a DM basis, while Ca-DPS had the lowest (3.3 g kg^{-1}). Biochar had the highest concentration of heavy metals, as pyrolysis normally concentrates these elements in the biochar (Yuan et al., 2011). Although the DPS and DPS-derived biochar can be effectively used in agriculture because they contain several important micro- and macronutrients, they should only be used if heavy metals that accumulate in soil can be avoided (Dad et al., 2019).

3.2. Mineral fertiliser equivalence – nitrogen

In the N trial, there was a strong positive linear correlation between cumulative crop DM yield or N uptake and mineral N application rate for both ryegrass and spring wheat grain (Figs. S2 and S3). The DPS treatments produced significantly higher cumulative yields of ryegrass DM than the study control (no N treatment) (Table S3). Application rates of Al-DPS significantly impacted the cumulative yield of the ryegrass, but

Table 1
Soil texture and characteristics used in pot trial.

Clay	Silt	Fine Sand	Coarse Sand	Organic Matter	Total N	Total P	Total K	Total Al	Total Ca	Total Fe	Morgan's P	pH
%	%	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/l	
15.0	30.1	34.6	20.3	6.5	2700	582.2	2639.5	14190.6	1367.2	13143.1	1.9	5.8

Fig. 1. Glasshouse pot trial with ryegrass and spring wheat.

Table 2
Characteristics of bio-fertilisers used in the pot trial.

Parameters	Al-DPS	Ca-DPS	DPS-biochar
DM (% of wt.)	13.1	42.9	100
OM (% of DM)	75.5	16.6	
pH	7.7	12.4	
TN (g/kg)	71.6	12.1	19.4
NH_4–H (g/kg)	4.5	0.15	0.046
TP (g/kg)	39.7	3.3	52.3
TC (%)	36.2	18.4	28.4
C/N	5.1	15.2	14.6
K (g/kg)	10.5	1.5	14.7
Mg (g/kg)	4.7	2.7	8.0
S (g/kg)	8.1	4.3	7.1
Na (g/kg)	2.2	0.99	9.3
Ca (g/kg)	31.9	251.9	97.0
Cr (mg/kg)	5.8	6.3	25.7
Cu (mg/kg)	7.8	6.0	44.7
Ni (mg/kg)	2.5	26.5	13.8
Pb (mg/kg)	<2	<2	16.4
Zn (mg/kg)	199.6	17.4	269.6
Al (g/kg)	19.2	10.4	33.8
Fe (g/kg)	0.69	0.72	4.1
Co (mg/kg)	<0.3	0.72	2.6
Mo (mg/kg)	2.1	1.2	5.4
Mn (mg/kg)	38.8	65.0	251.2
Cd (mg/kg)	<0.15	0.39	0.29
As (mg/kg)	<1.5	<1.5	2.2
B (mg/l)	15.4	4.8	37.7
Se (mg/kg)	1.4	<1	<1

Table 3
Ryegrass and wheat grain pot trial results for bio-fertiliser type, rate applied in pot trial and % of mineral fertiliser equivalent value to guide agronomic advice.

Treatment	N rate	N-MFE from DM yield response curve Eqn. 1	N-MFE from N uptake response curve Eqn. 1	ANR from Eqn. 3	N-MFE from Eqn. 5
	kg ha^{-1}	%	%	%	%
Ryegrass					
Al-DPS	125	47.6	24.0	21.9	22.7
Al-DPS	160	66.1	38.8	35.6	39.9
Ca-DPS	125	77.4	17.0	15.4	16.0
Ca-DPS	160	62.8	30.0	27.5	30.8
Wheat grain					
Al-DPS	160	71.6	106.3	22.2	117.4
Al-DPS	240	85.2	76.5	16.2	63.5
Ca-DPS	160	143.9	90.8	18.3	96.7
Ca-DPS	240	57.3	56.5	11.1	43.7

	P rate	P-MFE from DM yield response curve Eqn. 2	P-MFE from P uptake response curve Eqn. 2	APR from Eqn. 4	P-MFE from Eqn. 6
	kg ha^{-1}	%[a]	%	%	%
Ryegrass					
Al-DPS	40	–	104.5	23.3	81.7
Al-DPS	80	–	62.5	13.5	71.8
Ca-DPS	40	–	23.6	8.6	30.0
Ca-DPS	80	–	−78.7	−12.2	−64.9
DPS-Biochar	40	–	25.6	8.9	31.3
DPS-Biochar	80	–	35.5	8.6	45.6
Wheat grain					
Al-DPS	50	–	110.0	6.7	74.8
Al-DPS	80	–	52.6	2.9	39.9
Ca-DPS	50	–	66.3	3.4	38.4
Ca-DPS	80	–	44.1	2.4	32.3
DPS-Biochar	50	–	17.7	−0.18	−2.0
DPS-Biochar	80	–	−0.46	−0.98	−13.4

[a] Crop yield is unresponsive to P application.

there was no difference in cumulative yield at either application rate for the Ca-DPS (Table S3). Compared to Al-DPS, the Ca-DPS applications produced a significantly lower yield at the first harvest, but this trend was reversed in the third and fourth harvests. A similar trend was found for the N uptake of Ca-DPS applications. For spring wheat, there were no significant differences between chaff or grain yields at either application rate of the two DPS treatments (Table S4).

Increased application rates of Al-DPS produced increases in cumulative N uptake in the ryegrass, but application rates of Ca-DPS had no significant impact on cumulative N update (Table S3). For spring wheat, there was no significant difference between N uptake in the wheat grain at either application rate of the two DPS treatments (Table S4).

Depending on the method of calculation (ANR, N-MFE based on DM yield or N uptake rate), there were large differences in equivalencies (Table 3). The N-MFE based on DM yield (ranging from 47.6% to 77.4% for ryegrass and 57.3%–143.9% for spring wheat grain) was much higher than the N-MFE based on N uptake (ranging from 17.0% to 38.8% for ryegrass and 56.5%–90.8% for spring wheat grain). Previous studies also reported that increasing N fertilisation significantly increased crop yield (Dad et al., 2019; Ghimire et al., 2021). This was because crop yield is strongly connected to rates of N fertilisation (Dong and Lin, 2020), while N uptake of crops can be affected by several factors such as type of organic fertilisers, N mineralisation, application rate and soil

properties (Rigby et al., 2016).

When N-MFE was calculated based on DM, yields of ryegrass and wheat grain increased proportionally to the applications of Al-DPS, but Ca-DPS yields were inverse to the applications. Similar trends were noted when N-MFE was calculated based on N uptake. This may be due to the high Ca concentrations in the Ca-DPS (almost eight times higher

than Al-DPS; Table 2), which may have impacted the absorption and utilisation of P and Mg by crops (Staugaitis and Rutkauskiene, 2012; Nest et al., 2021).

Since the ultimate goal of fertilisation is to increase yield, and not nutrient concentration, of the crop, the N-MFE based on DM yield is important for farmers to help them improve crop yield when they using DPS. This value is often underestimated in pot experiments, as the unhindered growth of plant roots is restricted by the physical boundaries of the pot (Kratz et al., 2019). There was no significant difference between the two methods used to calculate N-MFE based on N uptake ($P > 0.05$), indicating that experiments for MFE measurement may be simplified with one mineral N fertiliser as reference.

N-MFE based on N uptake can vary widely as N uptake from organic fertilisers depends on many factors, such as the mineralizable N fraction, which is strongly connected to the different types and sources of organic fertilisers (Rigby et al., 2016). The NH_4–N content in organic fertilisers is one of the major inorganic N forms that can be directly absorbed by plant roots (Pierzynski et al., 2005). Nitrogen mineralisation is also largely dependent on the C:N ratio, because it is stoichiometrically linked with the requirement of saprophytic microbes (Manzoni et al., 2008). The C:N ratio of the two DPS samples used in this study was below 30, which means that organic N was readily mineralised at increasing rates (Bonanomi et al., 2019). Therefore, as the Al-DPS contained a higher NH_4–N content (6.4% of TN) than the Ca-DPS (1.3% of TN) and had a lower C:N ratio (5.1) than the Ca-DPS (15.2), it provided more plant available N and higher N-MFE at the same application rate. Likewise, in the study of Ashekuzzaman et al. (2021b), a higher N-MFE for N uptake in ryegrass was found with Fe-DPS containing a larger proportion of mineral N content than with lime-treated sludge. For ryegrass, both DPS applications had the higher ANR and N-MFE, because higher N application rates promotes crop yield and N uptake (Wang et al., 2010). Conversely, higher application rates resulted in lower ANR and N-MFE for spring wheat grain. This implied that DPS application at a rate of 240 kg N ha^{-1} for spring wheat exceeded the N requirements for maximum plant N uptake.

3.3. Mineral fertiliser equivalence – phosphorus

The cumulative ryegrass P uptake and spring wheat grain P uptake had a positive linear correlation with mineral P fertiliser rate (Fig. S4). In the ryegrass trial, there was no significant difference between the cumulative yields of the control (no P treatment) and Al-DPS, Ca-DPS or biochar treatments at the 40 kg ha^{-1} application rates (Table S5). Application rate did not affect the cumulative yield for any treatment (except for Ca-DPS applied at 80 kg ha^{-1}, which produced a lower yield than the 40 kg ha^{-1} application rate). With the exception of Ca-DPS, applied at 80 kg ha^{-1}, there was no significant difference in cumulative yields of ryegrass between the reference fertiliser and treatments. Similar trends were noted in the spring wheat, where there was no significant difference between the chuff and grain yields of the control and all treatments (Table S6). Application rate did not impact yield and there was no significant difference between the reference fertiliser and treatments. The Ca-DPS yield and P uptake in the first and second harvest of ryegrass were significantly lower than the other treatments (the ryegrass yield in the first harvest was so low that it was impossible to conduct P analysis on the biomass).

For both the ryegrass and spring wheat, DPS and biochar application rate did not impact the cumulative P uptake, with the only exception being the Ca-DPS application to ryegrass, in which the higher application rate of 80 kg ha^{-1} produced a lower cumulative P uptake than 40 kg ha^{-1}. In the case of the spring wheat, there was no significant difference between the cumulative P uptake in either the chuff or grain and the control.

The P-MFE results using the two methods are presented in Table 3. There was no significant difference between the two methods ($P > 0.05$). Numerous bioassay studies (Ashekuzzaman et al., 2021b; Kratz et al., 2017; Xin et al., 2017) used both crop yield and P uptake as indicators for P availability. Yield is much easier to measure than P uptake, because the latter requires chemical analyses. However, yield is not as sensitive as P uptake (Kratz et al., 2019). In this study, types and rates of fertiliser had no significant effect on plant yields, which was also observed by Wang et al. (2012) and Ashekuzzaman et al. (2021b). In contrast, P uptake was more sensitive to the P source, and is therefore considered a more valid indicator of available P. It should be noted that in pot trials the operating assumption is that the source of available P in bio-based materials is 100% available. This may be the case in mineral fertilisers as P is immediately incorporated into the soil-crop system, but this is certainly not the case for bio-fertilisers. The work of Khomenko et al. (submitted) indicates that DPS as a source of P must go through some form of mineralisation before it can be considered as available as chemical P. For example, utilisation of phosphate solubilising microorganisms can convert insoluble P to soluble forms (HPO_4^{2-}, $H_2PO_4^-$) and degrade high molecular-weight phosphate, which increases plant available P content in the soil (Alori et al., 2017).

The P-MFE of DPS and DPS-Biochar ranged from −78.7% to 104.5% for ryegrass and −13.4%–110.0% for spring wheat grain (Table 3). Al-DPS treatments had the highest P-MFE among all the types of fertilisers examined in this study. Compared with Ca-DPS, Al-DPS contained higher OM content (Table 2), which may increase P solubility, decrease P fixation and therefore significantly improve P availability to plants (Bhattacharyya et al., 2015). Ca-DPS in this study also had high pH and the soils treated by Ca-DPS became alkaline by the end of the study (from 5.8 to 7.8 ± 0.1). A molar Ca:P ratio of 2 in bio-fertilisers also can negatively affect P availability for plant uptake due to the formation of low soluble Ca–P compounds such as hydroxyl-apatite (Nest et al., 2021). In this study, the molar Ca:P ratio of Ca-DPS was extremely high (106), indicating that P in Ca-DPS was unavailable to crops.

The negative P-MFE value in DPS-biochar treatments for spring wheat implied slow P release and low crop P uptake as compared to the no P treatment soil. Biochar is a stable form of carbon that is difficult to break into components (William and Qureshi, 2015), so that less nutrients may be released for plant utilisation. While losses of P during pyrolysis are negligible, P is converted into more stable, less available forms such as Mg or Ca minerals. Therefore, biochar creates a more permanent nutrient pool for long-term nutrient uptake by crops (Frišták et al., 2018). Chow and Pan (2020) also found that the fertiliser effect of biochar on the carrot and choy sum growth was not as good as that of the other organic fertilisers including biosolids, chicken manure and food waste compost.

3.4. Implications of the research

As a relatively new waste type used by farmers, DPS is perceived as a "cleaner" fertiliser source than biosolids derived from human sewage sludge (Ashekuzzaman et al., 2021a; Hu et al., 2021). A MFE determination of DPS can quantify its fertiliser value and provide sound advice to farmers pertaining to its sustainable use, as well as promoting its use as an alternative bio-fertiliser. In this study, Al-DPS had the highest MFE, when quantified in terms of N and P application rates. However, based on the significantly higher ryegrass yield and nutrient uptake in the last two harvests, Ca-DPS may have potentially good long-term fertiliser replacement value. Long-term pot or field trials provide more information on the fertiliser value of these products. While DPS-biochar had poor MFE, it can also perform other roles such as an amendment to improve soil properties (Laird et al., 2010). Future research must include more types of STRUBIAS products in the both pot and field trials, and must focus on their P bioavailability and P-MFE as they are secondary materials of P recovery. Little information on P transformations during the generation of STRUBIAS products and the effect of these treatments on P bioavailability is available at present. Knowledge of the amount of available P in DPS-derived STRUBIAS products is essential to determine the optimal rate to be applied to meet crop P requirements, while

ensuring a low risk of over-fertilisation (Plaza et al., 2007).

4. Conclusions

This study quantified the mineral fertiliser equivalent value of two types of DPS (Al-DPS and Ca-DPS) and a DPS-derived biochar in a six-month pot trial. Al-DPS had the highest N- and P-MFE, indicating that it had the best fertiliser value. However, Ca-DPS has long-term potential to be a good alternative fertiliser due to high yield and nutrient uptake in the last harvest of ryegrass. DPS-biochar had poor P-MFE, indicating that its use as a fertiliser replacement is limited. The results of application rate and how it affects MFE outcomes were variable. High-rate applications of DPS only improved N-MFE of ryegrass, while N-MFE of spring wheat and P-MFE decreased with higher application rates. This indicated that over-fertilisation was unnecessary and should be avoided. There was no significant difference between two different calculation methods (from response curve and apparent nutrient recovery value) for MFE. Calculations of N-MFE, based on DM yield and crop N uptake, are necessary, as the results can give different information for farmers to use these alternative fertilisers.

Credit author statement

W. Shi: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Validation; Visualization; Roles/Writing – original draft; Writing – review & editing. **M.G. Healy:** Conceptualization; Funding acquisition; Investigation; Methodology; Supervision; Validation; Visualization; Writing – review & editing. **S.M. Ashekuzzaman:** Conceptualization; Investigation; Methodology; Validation; Visualization;– review & editing. **K. Daly:** Conceptualization; Methodology; Validation; Visualization;– review & editing. **O. Fenton:** Conceptualization; Funding acquisition; Investigation; Methodology; Project administration; Resources; Supervision; Validation; Visualization; Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2022.116012.

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