MINERAL FERTILISER EQUIVALENCE VALUE OF DAIRY PROCESSING WASTE AND DERIVED STRUBIAS PRODUCTS

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DECLARATION

I declare that this dissertation entitled “Mineral fertiliser equivalence value of dairy processing waste and derived STRUBIAS products” is the result of my own work, except where explicitly stated otherwise, for which references are made. This thesis has not been submitted in whole or in part in support for another degree to any University or Institution.

Wenxuan Shi

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ABSTRACT

Globally, agriculture urgently needs alternative sources of phosphorus (P). Presently, global agriculture is over-reliant on inorganic mineral P fertilisers sourced from finite mining sources. This is especially relevant in the European Union (EU), since Europe lacks natural rock phosphate deposits. There are many alternative organic sources of P, which could be used at low cost in agriculture to grow crops. For example, as one of the largest agricultural-food sectors in EU, the dairy processing industry generates large amounts of P-rich dairy processing sludge (DPS), which can be further processed into secondary-raw-material-based fertilising products, referred to as STRUBIAS (STRUvite, BIochar, or incineration AShes). As DPS and DPS-derived STRUBIAS products have the potential to be used as bio-based fertilisers, to encourage farmers to choose such fertiliser alternatives and stimulate their access to the market, the EU has implemented changes to the Fertiliser Regulations. To date, few studies have focused on the potential of these products to be used as agricultural fertilisers, which has hindered their incorporation in agricultural nutrient management planning. This thesis aims to address the knowledge gaps associated with their agronomic performance and potential environmental risks when reused as fertilisers in agriculture. Specifically, the aims of this thesis were to: (1) quantify the nutrient and metal content of a range of DPS and DPS-derived products (2) compile a database and develop a MS Excel^{TM} calculator programme to provide farmers with a quick and safe way to reuse these products (3) determine the mineral fertiliser equivalent value (MFE) of a range of these products when used to grow ryegrass and spring wheat, and (4) examine how the different application rate (optimal versus high) and calculation methods (with and without chemical fertiliser response curves) affect MFE results, which, in turn, will enable a standard approach to be used in fertilisation.

Three types of DPS (activated sludge aluminum-precipitated DPS (Al-DPS), activated sludge iron-precipitated DPS (Fe-DPS), and lime-stabilised sludge calcium-precipitated DPS (Ca-DPS) were collected from dairy factories in Ireland. In addition, three types of STRUBIAS products (struvite, chars, and ash) were created in collaboration with project partners (EU REFLOW ITN) for use in the present study. Physical and chemical characterisation of these samples showed that all the products had high P content but low heavy metal content, indicating their good agronomic performance potential.

The generation of these data also enabled the creation of a maximum legal land application rate calculator (in MS Excel^{TM} format) for raw DPS and DPS-derived STRUBIAS products. This utilises the characterisation data, together with crop-specific data and site-specific soil P content, to calculate safe application rates based on nutrient or metal contents and limits for soil. This tool is adaptable for any crop and will enable both agronomic and environmental goals to be achieved when using these products.

This calculator was also used to calculate application rates for a 6-month pot experiment using ryegrass and spring wheat, wherein the MFE of ranges of DPS and DPS-derived STRUBIAS products was quantified for the first time. The dry mass and nutrient content of harvested crops were used to calculate the MFE of the DPS and STRUBIAS products. The results indicated that not all these products were suitable for use as bio-based fertilisers. Only Al-DPS and three of the four struvites had good agronomic performance, the best being Al-DPS (the N-MFE ranged from 22.7 to 117.4% and the P-MFE ranged from 39.9 to 110.0%). The low agronomic performance of some products could be explained by processing activity data.

Arising from the findings of this thesis, DPS and DPS-derived products show promise as fertilisers. However, some will benefit from processing changes that will avoid some of the current fertiliser limitations. There needs to be more transparency with respect to how MFE is calculated. As there is currently no standard method to assess the agronomic performance of products and a lack of transparency when the MFE is documented, advisors or growers should ask for more information before recommending products to farmers. The work undertaken in this thesis needs to be also undertaken at field-scale with different soil and crop types.

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Abbreviations

A1	Ash sample
ACS	American Chemical Society
AC sludge	Bio-chemically treated activated sludge
Al	Aluminium
Al-DPS	Activated sludge aluminum-precipitated
Al-PC2	Pyrochar produced from Al-DPS at 450°C
Al-PC3	Pyrochar produced from Al-DPS at 700°C
ANOVA	Analysis of variance
ANR	Apparent N recovery
$ANR_{Reference}$	Apparent N recovery of mineral N fertiliser
$ANR_{Treatment}$	Apparent N recovery of organic residues
AOP	Advanced oxidation processes
APR	Apparent P recovery
$APR_{Reference}$	Apparent P recovery of mineral P fertiliser
$APR_{Treatment}$	Apparent P recovery of organic residues
As	Arsenic
B	Boron
BOD_5	Biological oxygen demand for 5 days
C	Carbon
Ca	Calcium
Ca-DPS	Lime-stabilised sludge calcium-precipitated
CaMAP	Struvite produced from dairy processing wastewater
CAN	Calcium ammonium nitrate
Cd	Cadmium

CIP	Clean-in-place
Cl_2	Chlorine gas
ClO_2	Dioxide
ClO^-	Chlorhexidine and hypochlorite
CMC	Component materials categories
Co	Cobalt
COD	Chemical oxygen demand
Cr	Chromium
Cu	Copper
DAF	Dissolved air floatation
DAF sludge	Lime treated dissolved air flotation processing sludge
DBPs	Disinfection by-products
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DM	Dry matter
DOM	Dissolved organic matter
DPS	Dairy processing sludge
dw	Dry weight
EBPR	Enhanced biological phosphorus removal
EC	European Commission
EDTA	Ethylenediaminetetraacetic acid
$EQ_{\text{mineral N or P fertiliser rate}}$	Equivalent amount of mineral N or P fertiliser that gives the same reference response compared to DPS
EU	European Union
Fe	Iron

Fe-DPS	Activated sludge iron-precipitated
Fe-HC1	Hydrochar produced by an iron-rich dairy processing sludge with no additional water
Fe-HC2	Hydrochar produced by an iron-rich dairy processing sludge with the addition of 1% H_2SO_4 to achieve moisture contents of 85%
Fe-HC3	Hydrochar produced by an iron-rich dairy processing sludge with the addition of 1% H_2SO_4 to achieve moisture contents of 90%
FEV	Fertiliser equivalency value
FEV-N	Fertiliser equivalent value of nitrogen
FEV-P	Fertiliser equivalent value of phosphorus
FOG	Fat, oil and grease
HAAs	Haloacetic acids
HC	Hydrochar
HC1	Hydrochar1 produced by an iron-rich dairy processing sludge with no additional water
HC2	Hydrochar2 produced by an iron-rich dairy processing sludge with the addition of 1% H_2SO_4 to achieve moisture contents of 85%
HC3	Hydrochar3 produced by an iron-rich dairy processing sludge with the addition of 1% H_2SO_4 to achieve moisture contents of 90%
Hg	Mercury
HTC	Hydrothermal carbonisation

ICP-AFS	Inductively coupled plasma atomic fluorescence spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectrometer
K	Potassium
K_{sp}	Water solubility
LSD	Least Significant Difference
MAP	magnesium ammonium phosphate
MAP1	Struvite produced from dairy processing wastewater
MAP2	Struvite produced from dairy processing wastewater
MCPA	2-methyl-4-chlorophenoxyacetic acid
MFE	Mineral fertiliser equivalent value
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
MOP	Potassium chloride
N	Nitrogen
N-MFE	Nitrogen mineral fertiliser equivalent value
n.a.	Not available
Na	Sodium
$N_{applied}$	Application rate of N
NH_3	Ammonia
NH_4	Ammonium
NH_4-N	Ammonium-N
Ni	Nickel
NO_2-N	Nitrite nitrogen
NO_3-N	Nitrate nitrogen

NPs	Nanoparticles
N $\text{uptake}_{\text{Control}}$	N uptake in the unfertilisered pots
N $\text{uptake}_{\text{Treatment}}$	N uptake in the fertilisered pots
OM	Organic matter
P	Phosphorus
P-MFE	Phosphorus mineral fertiliser equivalent value
P_{applied}	Application rate of P
PAHs	Polycyclic aromatic hydrocarbons
Pb	Lead
PC1	Pyrochar produced from a mixture of DPS and wood chips
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and dibenzofurans
P_{NAC}	Phosphorus in neutral ammonium citrate
P_{NAC}-solubility	Solubility of phosphorus in neutral ammonium citrate
POPs	Persistent organic pollutants
P $\text{uptake}_{\text{Control}}$	P uptake in the unfertilisered pots
P $\text{uptake}_{\text{Treatment}}$	P uptake in the fertilisered pots
S	Sulphur
S1	Struvite1 produced from dairy processing wastewater
S2	Struvite2 produced from dairy processing wastewater
S3	Struvite3 produced from dairy processing wastewater
S4	Struvite4 produced from HTC liquor
SAS	Statistical Analysis System
Se	Selenium
SOP	Sulphate of potash

SP	Super phosphate
SSA	Specific surface area
STRUBIAS	STRUvite, BIochar, or incineration AShes
TC	Total carbon
TEQs	Toxic equivalent
THMs	Trihalomethanes
TN	Total nitrogen
TON	Total oxidised nitrogen
TP	Total phosphorus
TS	Total solids
TSS	Total suspended solids
UHT	Ultra-high-temperature
VS	Volatile solids
VSS	Volatile suspended solids
WHC	Water holding capacity
WWTPs	Wastewater treatment plants
Zn	Zinc

Chapter 1 Introduction

1.1 Overview

Phosphorus (P) is essential for life, but it is a finite resource. The scarcity and unequal global distribution of P represent a serious “P challenge” (Chiders et al., 2011), particularly as primary world P reserves may be exhausted within 50-400 years (van Dijk et al., 2016). As Europe lacks natural P rock deposits and mainly depends on imported P, alternative sources to rock phosphate are urgently needed.

The dairy industry is the European Union’s (EU) largest industrial food wastewater contributor and one of the main sources of P-rich industrial effluent (Augère-Granier, 2018). The abolition of EU milk quotas in 2015 resulted in a 2.8% annual growth in milk production, which gave rise to the generation of P-rich dairy wastewater and effluents. To meet discharge limits, dairy wastewater must be treated before discharge. A large volume of solid organic wastes, referred to as dairy processing sludge (DPS), are generated when conventional wastewater treatment systems are used (Ashekuzzaman et al., 2019a). The EU, through its Circular Economy policy, has prioritised the recovery and safe reuse of plant bioavailable P from food and municipal waste streams in order to add resilience in the event of disruption of supply, while simultaneously mitigating the environmental consequences of P leakage (EC, 2015). Recycling or reuse of DPS to replace other resources is the best solution for the disposal and recovery of valuable fertiliser components (Ashekuzzaman et al., 2019b; Uysal and Kuru, 2015). This is one of the main building blocks of the EU Green Deal (Fetting, 2020) and will contribute to both bioeconomy and circular economy. Different parts of the green economy are explained in Figure 1.1.

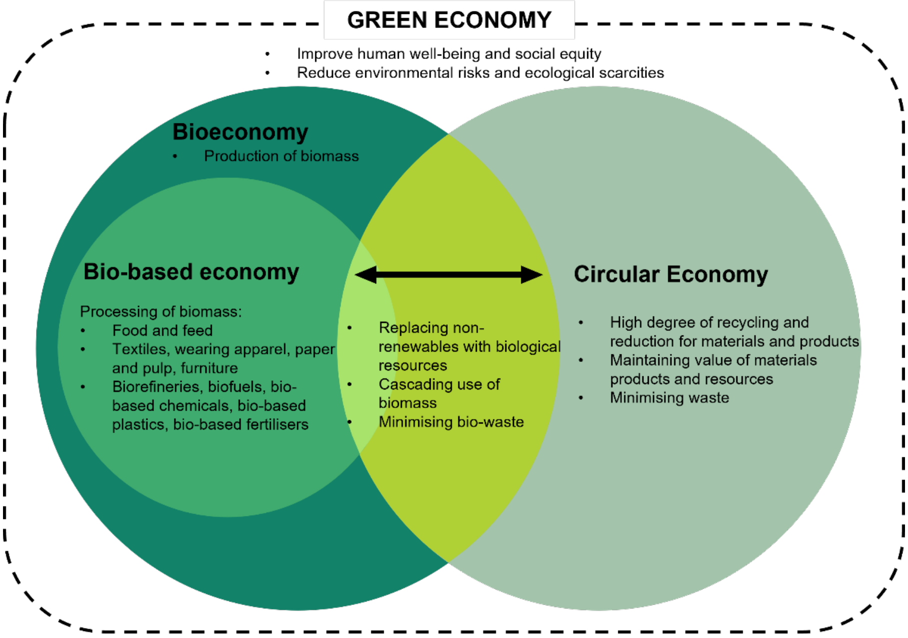


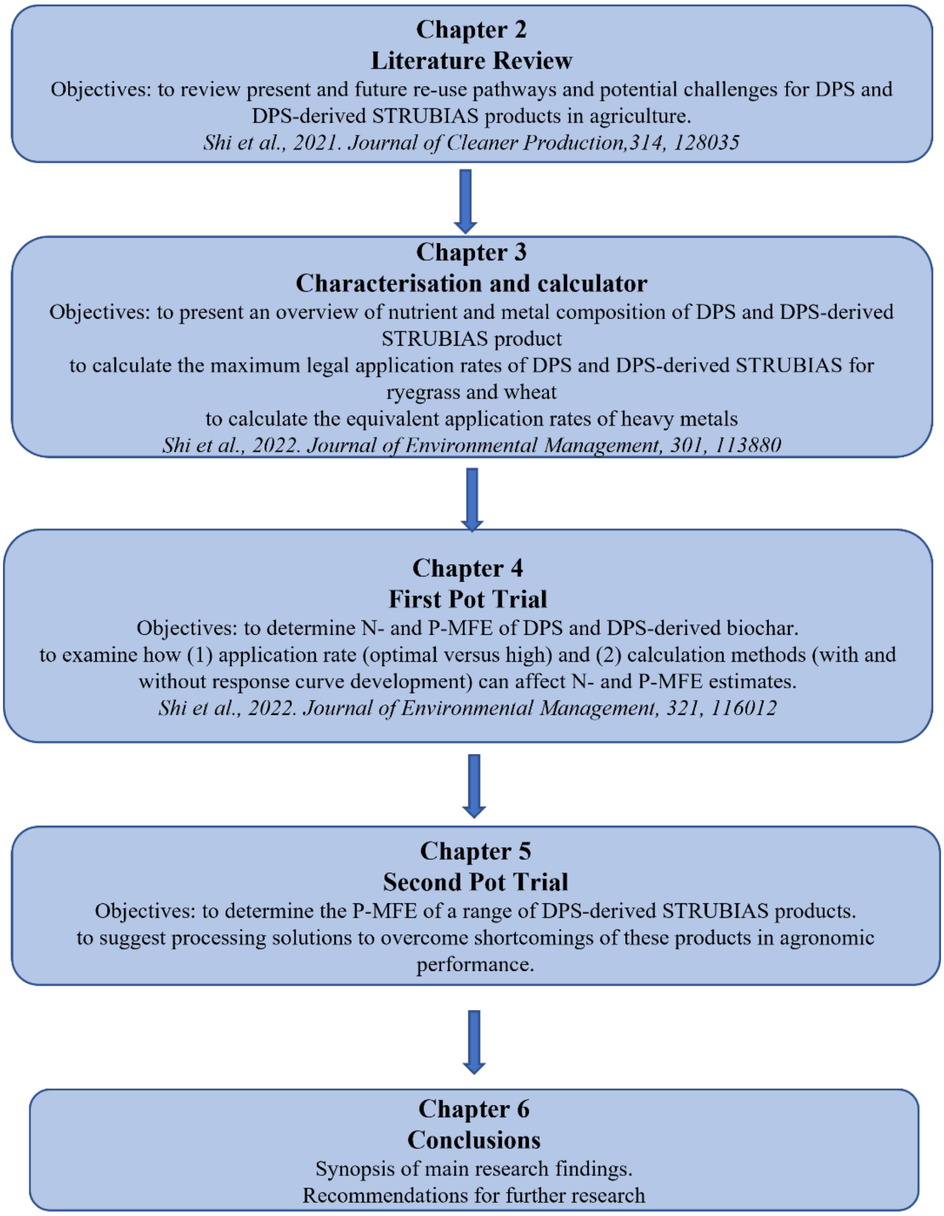
Figure 1.1 Relationships between bioeconomy, bio-based economy, green economy, and circular economy (adapted from Košir et al., 2021).

According to current practices in the EU, DPS is categorised as a biosolid (Pankakoski et al., 2000), and therefore can be spread on agricultural lands (arable and grassland) as it is assumed to be rich in both the macro- and micro-nutrients, which are required for healthy plant and animal growth (Ryan and Walsh, 2016). Other than direct land spreading, reusing P from DPS has been hampered by lack of information regarding its agronomic value, environmental risks, lack of available technology, suitably trained personnel, and a market for the products. To stimulate innovation in technologies for producing substitutes for mined phosphate rock from P-rich wastes, the EU has implemented changes to the Fertiliser Regulations, which permit CE labelling (CE labelling means that products may be sold in the EU) of waste-based fertilisers in order to ease their access to the single market (EC, 2019). This opens opportunities for the dairy processing industry to innovate by adapting technologies and new waste management strategies to minimise P leakage while benefiting from emerging market opportunities. DPS can be processed further into secondary-raw-material-based fertilising products, referred to as STRUBIAS (STRUvite, BIochar, or incineration AShes) (Huygens et al., 2018). STRUBIAS products stemming from many sources have already been recognised as fertilisers by EU and are expected to be on the EU fertiliser market by 2030 as safe and effective alternatives for mined rock phosphate (Huygens et al., 2018; EC, 2019).

The dairy processing industry in Ireland generates huge volumes of nutrient rich DPS, which currently goes to land. However, as DPS is a somewhat new alternative fertiliser, few studies have quantified the agronomic performance of DPS and DPS-derived STRUBIAS products specifically. Therefore crucial knowledge gaps prevent these products from being recognised as sustainable marketable products. For example, few studies have examined the nutrient and metal profiles of these products (which vary across processing plant, technologies, type, and seasonally). The potential presence of toxic metals and/or emerging contaminants in these products may cause problems for agricultural lands (Hu et al., 2021). The mineral fertiliser equivalent value (MFE), which is an important parameter for farmers and agricultural advisors to achieve both agronomic and environmental goals, is not quantified and only default values are used in nutrient management plans based on ad-hoc testing or on other products. Therefore, more studies should be conducted across the DPS from different factories to avoid improper landspreading and environmental risk. A thorough investigation and creation of a calculator that enables calculation of permissible application rates of these products in the context of EU soil and fertiliser regulations (Ulrich, 2019) is needed.

1.2 Thesis structure and objectives

A flowchart indicating the structure of this thesis is given in Figure 1.2. In Chapter 2 a review of present and future re-use pathways of DPS and DPS-derived STRUBIAS is presented. In this chapter, nutrient and metal data, MFE studies, potential emerging contaminants, and technologies to process STRUBIAS products are reviewed. In Chapter 3 the nutrient and metal composition of DPS and DPS-derived products are presented and a calculator that enables calculation of permissible application rates of these products in the context of EU soil and fertiliser regulations is developed. In Chapter 4, the nitrogen (N) and P mineral fertiliser equivalent values (N- and P-MFE) of two DPS and one DPS-derived biochar are determined in ryegrass and spring wheat growth trials. In Chapter 5 the P-MFE of a range of DPS-derived STRUBIAS products is also determined using a method similar to Chapter 4. Finally, the overall conclusions of these chapters are addressed in Chapter 7, with recommendations for further research.



Chapter 2
Literature Review
Objectives: to review present and future re-use pathways and potential challenges for DPS and DPS-derived STRUBIAS products in agriculture.
Shi et al., 2021. Journal of Cleaner Production,314, 128035

Chapter 3
Characterisation and calculator
Objectives: to present an overview of nutrient and metal composition of DPS and DPS-derived STRUBIAS product
to calculate the maximum legal application rates of DPS and DPS-derived STRUBIAS for ryegrass and wheat
to calculate the equivalent application rates of heavy metals
Shi et al., 2022. Journal of Environmental Management, 301, 113880

Chapter 4
First Pot Trial
Objectives: to determine N- and P-MFE of DPS and DPS-derived biochar.
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.
Shi et al., 2022. Journal of Environmental Management, 321, 116012

Chapter 5
Second Pot Trial
Objectives: to determine the P-MFE of a range of DPS-derived STRUBIAS products.
to suggest processing solutions to overcome shortcomings of these products in agronomic performance.

Chapter 6
Conclusions
Synopsis of main research findings.
Recommendations for further research

Figure 1.2 Flowchart of thesis structure including study objectives.

1.3 Contribution to existing knowledge

1.3.1 Peer-reviewed publications (published)

To date, three peer review papers have been published from this work, based on Chapter 2, 3 and 4, respectively:

Shi, W., Healy, M. G., Ashekuzzaman, S. M., Daly, K., Leahy, J. J., Fenton, O., 2021. Dairy processing sludge and co-products: A review of present and future re-use pathways in agriculture. Journal of Cleaner Production, 314, 128035. https://doi.org/10.1016/j.jclepro.2021.128035

Shi, W., Fenton, O., Ashekuzzaman, S. M., Daly, K., Leahy, J. J., Khalaf, N., Y. Hu., K. Chojnacka., C. Numviyimana., Healy, M. G., 2022. An examination of maximum legal application rates of dairy processing and associated STRUBIAS fertilising products in agriculture. Journal of Environmental Management, 301, 113880. https://doi.org/10.1016/j.jenvman.2021.113880

Shi, W., Healy, M. G., Ashekuzzaman, S. M., Daly, K., Fenton, O., 2022. Mineral fertiliser equivalent value of dairy processing sludge and derived biochar using ryegrass (Lolium perenne L.) and spring wheat (Triticum aestivum). Journal of Environmental Management, 321, 116012. https://doi.org/10.1016/j.jenvman.2022.116012

A manuscript based on Chapter 5 is currently under review.

In addition, two papers have been published as part of the "EU REFLOW ITN" project (the EU-funded project of which this work forms a part), which reviews the state of knowledge about DPS and DPS-derived STRUBIAS fertilisers:

Hu, Y., Khomenko, O., **Shi, W**., Velasco Sanchez, A., Ashekuzzaman, S. M., Bennegadi-Laurent, N., Daly, K., Fenton, O., Healy, M. G., Leahy, J. J., Sørensen, P., Sommer, S. G., Taghizadeh-Toosi, A., Trinsoutrot-Gattin, I. 2021. Systematic Review of Dairy Processing Sludge and Secondary STRUBIAS Products Used in Agriculture. Frontiers in Sustainable Food Systems, 386. https://doi: 10.3389/fsufs.2021.763020

Khalaf, N., **Shi, W**., Fenton, O., Kwapinski, W., Leahy, J. J. 2022. Hydrothermal carbonization (HTC) of dairy waste: effect of temperature and initial acidity on the composition and quality of solid and liquid products. Open Research Europe. Jul 12;2:83. https://doi.org/10.12688/openreseurope.14863.1

The published journal papers are presented in Appendix A.

1.3.2 Poster presentations

Shi, W., Healy, M. G., Ashekuzzaman, S. M., Daly, K., Fenton, O. Safe Use of Dairy Processing Sludge and STRUBIAS Food System Fertilising Products in Agriculture. AGU Fall Meeting. Dec. 13-17, 2021. New Orleans, US.

Shi, W., Healy, M. G., Ashekuzzaman, S. M., Daly, K., Fenton, O. Safe Use of Dairy Processing Sludge and STRUBIAS Food System Fertilising Products in Agriculture. The International Fertiliser Society Agronomic Conference. Dec. 9-10, 2021. Cambridge, UK.

1.3.3 Oral presentations

REFLOW-ITN Network Management Committee Meetings:

- Online, March 2020
- Online, October 2021
- France, Rouen, May 2022

One health day annual conference, Galway, Ireland, Nov 2021

5th Phosphorus in Europe Research Meeting (PERM5), Vienna, Austria, June 2022

1.4 REFLOW- Innovative Training Network Marie Curie Action H2020

Network-wide training and skill development

1.4.1 Secondments to partner organisations

March-May 2022, Aarhus University, Aarhus, Denmark

February-March, July-August 2022, University of Galway, Galway, Ireland

1.4.2 Seasonal Schools

SS1: Summer School on fundamentals of research practices, March 2020, online

SS2: Summer School on maximising research impact, October 2021, Vic, Spain

SS3: Summer School on science to policy (translational science), May 2022, Rouen, France

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Hu, Y., Khomenko, O., Shi, W., Velasco Sanchez, A., Ashekuzzaman, S. M., Bennegadi-Laurent, N., Daly, K., Fenton, O., Healy, M. G., Leahy, J. J., Sørensen, P., Sommer, S. G., Taghizadeh-Toosi, A., Trinsoutrot-Gattin, I., 2021. Systematic Review of Dairy Processing Sludge and Secondary STRUBIAS Products Used in Agriculture. Frontiers in Sustainable Food Systems, 386. https://doi: 10.3389/fsufs.2021.763020

Huygens, D., Saveyn, H., Tonini, D., Eder, P., Sancho, L. D., 2018. Pre-final STRUBIAS Report, DRAFT STRUBIAS recovery rules and market study for precipitated phosphate salts and derivates, thermal, oxidation materials and derivates and pyrolysis and gasification materials in view of their possible inclusion as component material categories in the revised fertiliser regulation. Circular Economy and Industrial Leadership Unit, Directorate B-growth and Innovation. https://phosphorusplatform.eu/images/download/STRUBIAS-Pre-Final-Report-circulated-13-8-18-p1-report.pdf

Košir, L. G., Sakellaris, G., Popp, J., Zimniewska, M., & Värnik, R. Monography: Bioeast Foresight Exercise: Sustainable Bioeconomies towards 2050, European Commission and Hungarian Ministry of Agriculture, October 2021.

Pankakoski, M., Noicol, R., Kestens, H., Bertsch, R., Coldewey, I., Hannemann, H., Kofoed, B., Carballo, J., Merilainen, V., Hale, N., Israilides, C., Moloney, A.M., Odlum, C., Sorilini, C., Kasai, N., Hiddink, J., Barnett, J.W., Sayler, A.R., Duddleston, W., Van Der Walt, H.S., Brits, T.J., 2000. A survey of the composition, treatment and disposal of sludge from dairy efuent treatment plants. Bulletin of the International Dairy Federation. 356, 4–34.

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Chapter 2 Dairy processing sludge and co-products: a review of present and future re-use pathways in agriculture

This chapter reviews present and future re-use pathways and potential challenges for dairy processing sludge and derived STRUBIAS products in agriculture. It has been published in the Journal of Cleaner Production (Shi et al., 2021. Dairy processing sludge and co-products: A review of present and future re-use pathways in agriculture, 314, 128035). Wenxuan Shi collected, reviewed, analysed and extracted relevant information from scientific papers, and is the primary author of this article.

Dairy processing sludge and co-products: a review of present and future re-use pathways in agriculture

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Abstract

The dairy industry is one of the largest global producers of wastewater and generates huge volumes of dairy processing sludge (DPS). There are two main types of DPS, lime-treated dissolved air floatation sludge and bio-chemically-treated activated sludge. These sludge types may also be converted to STRUBIAS (STRUvite, BIOchar, AShes) products which have potential as fertilisers, secondary feedstocks for phosphate fertiliser granules, and soil amendments. A small number of studies indicate that these products have variable nutrient and metal contents, which differ across sludge and STRUBIUS product types. This is due to many factors such as the type of dairy plants, wastewater treatment process and production technologies. Although such products are commonly applied to land, their phosphorus (P) and nitrogen (N) fertiliser equivalency values (FEV) are understudied at field scale. Their contaminants including heavy metals, antimicrobial drugs, hormones, pesticides, disinfectants, persistent organic pollutants (POPs), microplastics and nano particles require quantification, as do their impact on soil and plant materials, and potential environmental impacts. This paper outlines both the advantages and challenges for use of DPS and STRUBIAS products. Despite their potential use in agriculture, the characterisation, fertilising effects, environmental risks

and the production technologies across all types must be evaluated before they can be a marketable fertiliser product.

Keywords: dairy processing sludge; agriculture, emerging contaminants, phosphorus recovery

2.1 Introduction

In the aftermath of the COVID-19 pandemic and the associated economic downturn, the world's food system will be under threat and must become more sustainable and resilient (EC, 2020). The recently published Farm to Fork Strategy of the European Union (EU) aims to accelerate the transition to a sustainable food and agriculture system (EC, 2020). One of the recommended practices is to reduce excess fertilisation and to foster the recycling of nutrients from different kinds of organic waste as fertilisers. This will contribute to the delivery of the "zero pollution ambition" of the EU Green Deal (EC, 2020). The European Commission (EC) has recently revised the EU Fertiliser Regulation (EC, 2019), expanding its scope to include secondary-raw-material-based fertilising products to support the shift to sustainable agriculture and a "circular economy" (Huygens et al., 2018). In particular, the EU needs safe recycling sources of phosphorus (P), as Europe lacks natural phosphate rock deposits and mainly depends on imported P. Exploring alternatives to mineral P fertilisers and increased recycling of P may substantially contribute to the reduction of demand for fossil P resources and the dependency on the importation of P from other countries (Arenas-Montaño et al., 2021).

The reuse of raw materials that are now disposed of as waste is one of the key principles of sustainable agriculture and the circular economy. As one of the largest agricultural sectors in the EU (Augère-Granier, 2018), the dairy industry is now considered to be the largest global industrial food wastewater source and one of the main sources of P-rich industrial effluents (Kolev Slavov, 2017; Erkan et al., 2018). To meet discharge limits, dairy wastewater must be treated before discharge. It can be either discharged along with other wastewaters into municipal wastewater treatment plants (WWTPs) or treated on site if dairy plants have their own WWTP. As conventional wastewater treatment systems are used, a large volume of solid organic wastes is generated. These are referred to as dairy processing sludge (DPS) when the dairy wastewater is treated on site (Ashekuzzaman et al., 2019a).

According to current practices in the EU, DPS is categorised as a biosolid (Pankakoski et al., 2000), and therefore can be spread on agricultural lands (arable and grassland) as it is rich in both the macro- and micro-nutrients required for healthy plant and animal growth (Ryan and Walsh, 2016). It also has potential to be used as an additive in compost, animal feed, biofuel, or it may be dried and incinerated (Korsström and Lampi, 2001; Ryan and Walsh, 2016). However, very few studies focus on DPS specifically. The fertiliser value and the possible environmental risk of DPS have not been studied in any great detail, and such knowledge gaps prevent such products from being recognised as sustainable marketable products. For example, the fertiliser value of DPS, which is an important parameter for farmers and agricultural advisors to know before land application, is rarely reported. It is significantly affected by the type of dairy plants, e.g. cheese factories generally have 50% more P than fresh milk dairies (Kwapinska et al., 2019). Therefore, more studies and tests should be conducted across the DPS from different factories to avoid improper landspreading. Moreover, although the heavy metal concentration of DPS has been reported to be low (Kwapinska et al., 2018; Pankakoski et al., 2000), some emerging organic pollutants may be present in DPS due to their lipophilic properties. The contamination of the soil with these emerging compounds, as a result of the DPS application, could be transferred to the plants via the roots into different plant tissues (Navarro et al., 2017). This would discourage many food companies from using crops or products (e.g. grazing of animals) originating from land amended with DPS (Perkins, 2019).

There are also other concerns related to the use of DPS for land spreading. DPS decomposes quickly and releases strong odours due to high fat, oil and grease (FOG) and total suspended solids (TSS) content (Atallah et al., 2020; Bharati and Shinkar, 2013). Therefore, it cannot be stored for long periods and as the transport costs are high, it is commonly spread on lands in the vicinity of the dairy factories. Since the land bank of the nearby lands that can receive DPS is limited, it is easy to cause local oversupply of DPS, potentially leading to the accumulation of nutrients in soil, which may ultimately damage the aquatic ecosystem (Healy et al., 2016; Peyton et al., 2016). Weather conditions also constrain land spreading. For example, the land application of DPS is prohibited during the closed period over winter (i.e. hydrologically active period) in Ireland (S.I. No 378/2006). For these reasons, DPS cannot be fully utilised for land spreading. In the long term, there is a need to find alternative treatment and disposal methods of DPS. Secondary-raw-material-based fertilising products, which are referred to as STRUBIAS (STRUvite, BIochar, or incineration AShes), have already been recognised as fertilisers by EU to address this issue (EC, 2019; Huygens et al., 2018). STRUBIAS materials derived from wastewater and sludge are expected to be on the EU fertiliser market by 2030 and to be safe and effective alternatives for mined rock phosphate and processed P fertilisers (Huygens et al., 2018).

Knowledge gaps pertaining to present and future re-use of DPS and STRUBIAS products in agriculture still remain. Before these products can be deemed sustainable and safely used in agriculture, these aspects need to be reviewed and recommendations presented. Therefore, this paper aims to review present and future re-use pathways and potential challenges for these products in agriculture. Identification of such knowledge gaps will give the dairy processing and agricultural industries guidance on future research that is needed and may add value to the supply chain of the dairy production process.

2.2 Methodology

The review was carried out using scientific literature from databases and search engines including Google Scholar, American Chemical Society (ACS), Science Direct, Scopus, Springer Nature, Wiley and Web of Science. A detailed search of DPS and co-products reuse in agriculture in relevant literature was completed using the following keywords: dairy waste, dairy processing sludge, dairy wastewater treatment, STRUBIAS, struvite, sludge ash, biochar, fertiliser, fertiliser replacement/equivalent value, phosphorus, recovery, recycling, reuse, and emerging contaminants. Various combinations and derivations of the keywords were used.

As a result of these search criteria, 136 scientific papers were selected, from which about 45 % were published in the last 5 years and 70 % in the last 10 years. A deeper analysis was conducted on these papers and relevant information was extracted such as: dairy wastewater treatment methods, properties of DPS and current practices, fertiliser efficiency of DPS, potential environmental risk of DPS application, potential co-products derived from DPS and potential use in agriculture.

2.3 Dairy processing sludge characterisation

2.3.1 Current knowledge of dairy effluent nutrient and metal content

The dairy industry produces various products such as sterilised and pasteurised milk, yogurt, ice cream, butter, cheese, and milk powder, with different processes taking place such as pasteurization, coagulation, filtration, centrifugation and chilling (Carvalho et al., 2013). Dairy effluents vary significantly both in quantity and quality based on dairy factory characteristics (Janczukowicz et al., 2008) (Tables 2.1 and 2.2). The flow rates of dairy effluents vary due to scale, products, techniques, processes and equipment (Gutiérrez et al., 1991), and may also vary diurnally (Danalewich et al., 1998). Milk processing rates are typically higher in summer and lower in winter, and result in high seasonal variations in wastewater volume and properties (Janczukowicz et al., 2008). Moreover, the composition of these effluents varies greatly depending on the different types of products, system and operation methods (Carvalho et al., 2013). The effluent generally comprises dilutions of milk (or milk constituents including lactose, minerals, fat, whey and protein) lost in the technological cycles, starter cultures used in manufacturing, by-products (whey, milk and whey permeates), residues and contaminants from washing milk containers, equipment and floors, disinfectant applied in clean-in-place (CIP) processes, and other additives that may be used (Ahmad et al., 2019; Kolev Slavov, 2017). Dairy processing effluent is distinguished by high concentrations of organics and nutrients, and a pH varying from 4 to 12. Such a large variation of the pH is attributed to the use of acid and alkaline detergents and sanitizers for washing (Britz et al., 2006). The residues of milk and milk by-products in the waste stream result in higher nutrient and organic contents than those normally present in domestic wastewater (Booker et al., 1999). Suspended solids are derived from coagulated milk, cheese curd, or flavouring ingredients (Demirel et al., 2005). High concentrations of sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) have been measured in the wastewater, while heavy metals may be also present in low concentrations (Table 2.3).

Table 2.1 DPS generation (per unit volume/mass of processed milk) and disposal pathways in different countries.

Region	Water consumption	Effluents loads	DPS volume	Method of Disposal	Reference
EU	0.2-11 L/L processed milk	3×10^5-3×10^6 L (in a factory with capacity:10^6L milk/day)	1-3t dry matter sludge (in a factory with capacity: 10^6L milk/day)	Wastewater: drained to rivers sludge: land spread	Daufin et al. (2001)
EU	0.28-21.2 L/L processed milk	0.3-21.2 L/L processed milk	0.2-30 kg sludge/t processed milk	--	EC (2006)
Sweden	0.96-4.0 L/L processed milk	0.86-4.3 L/L processed milk	--	Landfill, compost, irrigation, biogas production. In Denmark, 2/3 sludge from dairies is irrigated on cultivated land and the rest is utilised in biogas production.	Korsström and Lampi (2001)
Denmark	0.60-1.9 L/L processed milk	0.75-1.5 L/L processed milk	--		
Finland	1.2-4.6 L/L processed milk	1.2-3.9 L/L processed milk	--		
Norway	2.5-6.3 L/L processed milk	2.0-3.3 L/L processed milk	--		
Ireland	2.3 L/L processed milk	2.71 ± 0.9 L/L processed milk	15–19.7 kg sludge/m^3 milk processed	Sludge: land spread (63%), compost (13.6%), or removed by licensed contractors (23.4%)	Ashekuzzaman et al. (2019a); Ryan and Walsh (2016)
Australia	0.07-2.90 L/L milk	--	31kg organic waste/t product	Compost, fertiliser, stockfeed and recovery of marketable products.	Prasad et al. (2004)
United States	--	0.10-12.4 L/L milk	--	Effluent: discharge into municipal sewage treatment system or irrigate on the land	Durham and Hourigan (2007)
UK	1.8 L/kg product	1-5 L/L processed milk	--	Sludge: landfilling	Klemes et al. (2008)

Table 2.2 Characteristics of dairy waste effluent.

Effluent type	pH	BOD_5 (g/L)	COD (g/L)	TS (g/L)	TSS (g/L)	VS (g/L)	VSS (g/L)	FOG (g/L)	TN (mg/L)	TP (mg/L)	DOM (mg/L)	Reference
Milk factory	5.5- 6.9	0.092-0.116	0.160-0.208	0.094-0.11							76.4-86.4	Mishra et al. (2000)
Dairy plants (produce cheese)	6.2- 11.3	0.565-5.72	0.785-7.62	1.84- 14.21	0.326-3.56	0.562-11.03	0.225-1.94		14 - 40	29-181		Danalewich et al. (1998)
Mixed dairy	4-11	0.24-5.9	0.5-10.4	0.71-7	0.06-5.8			0.02-1.92	10- 660	0-600		Kolev Slavov, (2017)
Milk reception	7.18	0.798	2.54		0.654			1.06				Janczukowicz et al. (2008)
Butter	12.08	2.42	8.93		5.07			2.88				Janczukowicz et al. (2008)
Cheese	7.90	3.46	11.75		0.940			0.331				Janczukowicz et al. (2008)
Cottage cheese	7.83	2.60	17.65		3.38			0.950				Janczukowicz et al. (2008)
Cheese whey	4.46	40	60	59	1.5							Gannoun et al. (2008)
Cheese whey	4.0-4.6	10-12.5	8.8-25.6	7.0- 8.3	1.6- 4.8			1.83- 3.76	310- 356	6.6-7.2		Rivas et al. (2010)
Hard cheese whey	5.80	29.48	73.45		7.15			0.994				Janczukowicz et al. (2008)
Cottage cheese whey	5.35	26.77	58.55		8.13			0.492				Janczukowicz et al. (2008)
Ice cream	5.2	2.45	5.2	3.9		2.6			60	14		Karadag et al. (2015)
Creamery	8-11	1.2-4	2-6		0.35-1		0.33-0.94		50-60			Demirel et al. (2005)
Cleaning water	10.37	3.47	14.64		3.82			3.11				Janczukowicz et al. (2008)

BOD_5=biological oxygen demand for 5 days, COD=chemical oxygen demand, TS=total solids, TSS=total suspended solids, VS=volatile solids, VSS=volatile suspended solids, FOG=fat, oil and grease, TN=total nitrogen, TP=total phosphorus, DOM=dissolved organic matter.

Table 2.3 Concentrations (mg/L) of trace elements in dairy waste effluent.

Effluent type	Cd	Fe	Cu	Pb	Zn	Ni	Na	K	Ca	Mg	Al	Co	Mn	Reference
Dairy plants (mainly produce yogurt)	0.090	1.181	0.350	1.095	0.234	0.166								Afolabi et al. (2015)
Creamery		2-5				0.5-1.0	170-200	35-40	35-40	5-8		0.05- 0.15	0.02- 0.10	Demirel et al. (2005)
Cheese		0.039- 4.33	0-0.03			0.012-0.071	263- 1265	8.6- 155.5	1.4- 58.5	6.5-46.3	0.06-0.26	0- 0.007	0- 0.835	Danalewich et al. (1998)
Mixed dairy		0.5-6.7				0-0.13	123-2324	8-160	11-120	2-97		0	0.03- 0.43	Demirel et al. (2005)

2.3.2 Current knowledge of DPS nutrient and metal content

Dairy wastewater must be treated to meet licensed discharge limits before discharge to surface water bodies. Normally, there are three main stages of wastewater treatment (Figure 2.1). Primary treatment consists of sedimentation/physical screening to remove large particles or debris, flow and composition balancing to stabilize effluent, chemical addition to control pH, and dissolved air floatation (DAF) to remove FOG (Ryan and Walsh, 2016). Two types of biological degradation systems, aerobic and anaerobic systems, can be used in secondary treatment to remove organic materials. Large quantities of DPS are produced during this stage and pollutants can be absorbed into onto the DPS surface. Aerobic biological techniques, including activated sludge process, sequencing batch reactors, bio-towers or membrane bioreactors, are carried out using dissolved oxygen (Ryan and Walsh, 2016). This is a reliable and cost-effective treatment in producing a high-quality effluent, but results in high DPS generation (0.6 kg dry DPS per kg of biochemical oxygen demand (BOD_5) removed) and costly disposal problems (Britz et al., 2006). Frequently used anaerobic biological technologies involve anaerobic lagoons, up-flow anaerobic sludge blankets, membrane anaerobic reactor systems, and completely stirred tank reactors (Britz et al., 2006). Less DPS is generated during anaerobic digestion than during aerobic processes (Britz et al., 2006). Phosphorus is removed in tertiary treatment through the use of chemicals like aluminium (Al) and/or iron (Fe) salts, before final discharge (Britz et al., 2006; Ryan and Walsh, 2016). Recently, the enhanced biological phosphorus removal (EBPR) process, without the need for chemical precipitants, has received increased attention. EBPR is achieved through the activated sludge process by recirculating sludge through anaerobic and aerobic conditions (Oehmen et al., 2007).

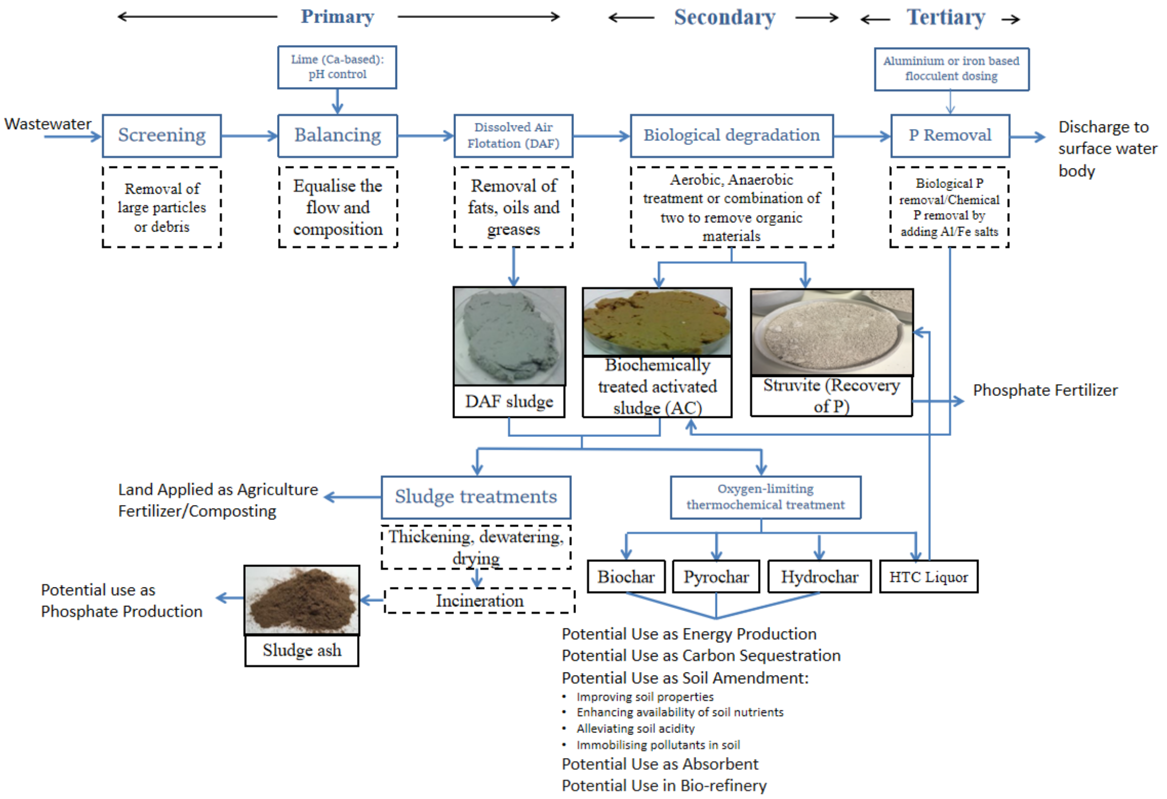

Figure 2.1 Flow chart of dairy wastewater treatment process and sludge, struvite, and char generation. DAF sludge=Lime treated dissolved air flotation processing sludge; AC sludge= Bio-chemically treated activated sludge (adapted from Ashekuzzaman et al. 2019a).

The wastewater treatment processes within a dairy processing plant generates a specific DPS type, which can be predominantly categorised into (1) lime-treated DAF sludge and (2) bio-chemically-treated activated sludge (Ashekuzzaman et al. 2019a). The former is produced after chemical and DAF treatment of raw wastewater during primary treatment. The latter is stabilized sludge from secondary biological degradation treatment, which can be either aerobic or anaerobic, or a combination of the two.

As DPS is categorised as a biosolid, it is commonly landspread in agricultural areas (Ryan and Walsh, 2016). DPS is a relatively new waste type and it is a much cleaner and valuable fertilising product than biosolids derived from sewage sludge, but it is rarely studied specifically. So far, very few studies have investigated the properties and fertilising effect of

DPS. López-Mosquera et al. (2000) used DPS as a fertiliser for grassland and found that the heavy metal content didn't lead to harmful accumulation of metals in the short- or medium-term (4 years) (Table 2.4). Ashekuzzaman et al. (2019a) collected and characterised 63 DPS samples covering 9 major dairy processing companies of Ireland and found that the nutrient content varied across different sludge types (Table 2.4). The reported values of heavy metals in DPS (Table 2.4) were found to be lower than the EU upper limit thresholds recommended for bio-based fertiliser (EC, 2019), which indicates their relatively low metal bioaccumulation risk if used in agriculture.

Table 2.4 Characteristics of DPS. Adapted from Ashekuzzaman et al. (2019a) and López-Mosquera et al. (2000).

Parameters	Bio-chemically treated activated sludge "AC"[*]	Lime treated DAF sludge "DAF"[*]	Combined treated sludge "CM"[a]	Anaerobically digested sludge "AD"	Dairy-plant sludge	EU requirements of bio-based fertiliser[b]
DM (% of wt.)	13.3	25.9	16.1	3.5±1.1		
OM (% of DM)	62.9	46.9	73.9	72.5±1.3		
pH	7.3	7.2	6.8	7.5±0.1		
TN (g/kg)	57.2	19.5	46.0	70.4±1.2		>10
TP (g/kg)	36.8	65.9	20.0	14.6±1.2		>10
TC (g/kg)	29.4	24.3	42.2	35.6±1.2		
K (g/kg)	7.2	3.9	2.9	6.1±1.1		>10
Mg (g/kg)	3.2	4.3	1.4	1.9±0.1		
S (g/kg)	4.8	2.1	7.6	5.3±0.7		
Na (g/kg)	5.3	3.5	3.6	19.9±3.0		
Ca (g/kg)	44.8	152.9	21.0	59.7±12.0		
Cr (mg/kg)	9.8	5.4	8.8	13.4±3.5	15.99±0.04	
Cu (mg/kg)	12.6	5.3	17.3	38.2±6.7	58.55±0.08	<300
Ni (mg/kg)	4.6	4.0	7.9	9.3±2.4	11.04±0.04	<50
Pb (mg/kg)	<2.0	<2.0	<2.0	6.3±2.9	10.05±0.12	<120
Zn (mg/kg)	75.2	54.7	109.8	217±46	289.74±0.67	<7800
Al (g/kg)	27.7	0.6	37.2	1.5±0.5		
Fe (g/kg)	1.5	1.1	1.8	0.7±0.1		
Co (mg/kg)	0.8	0.3	0.7	0.9±0.2		
Mo (mg/kg)	2.2	0.5	2.1	18.4±3.6		
Mn (mg/kg)	55.1	28.2	80.7	28.2±6.8		
Cd (mg/kg)					0.11±0.001	<1.5
Hg (mg/kg)					0.08±0.02	<1

DM=dry matter, OM=organic matter, TN=total nitrogen, TP=total phosphorus, TC=total carbon, n.a. = not available

[a] Median values are presented.

[b] The requirements of EU solid bio-based fertiliser with more than one macronutrients (EC, 2019).

2.4 Fertiliser equivalent value (FEV) of DPS

The efficiency of most bio-based fertiliers is normally unstable and lower than chemical fertilisers because of their relatively low nutrient content, slow nutrient release rate and highly variable nutrient composition (Chen, 2006). Therefore, the agronomic value of DPS should be determined before they are used in agriculture, which will make farmers more confident to use them. The FEV is defined as the application rate of mineral fertiliser to which the fertilisation effect of bio-based fertilisers on crop yield or nutrient uptake is equivalent (Brod et al., 2012).

The FEV can both provide a quantitative estimate of the amount of efficient nutrients in bio-based fertiliser and a theoretical estimate of its actual price in comparison to a mineral fertiliser. This can give farmers information about how to use bio-based fertilisers and the economic impacts associated with their use (Ashekuzzaman et al. 2019a). However, the results of FEV may vary widely, as FEV is not only affected by the assessment method, but also by factors like type of bio-based fertilisers, crop type, fertiliser application time (Delin, 2011), rates (Hijbeek et al., 2018), and method (Lalor et al., 2011).

To date, studies of FEV have mainly focused on the fertiliser equivalent value of nitrogen (N) (FEV-N) of manure and slurry. Research on the FEV (both FEV-N and fertiliser replacement value of P (FEV-P)) of DPS is scarce. Ashekuzzaman et al (2021) applied an agronomic trial in grassland with four representative DPS to determine both the FEV-N and FEV-P of DPS. The FEV-N of DPS samples was observed to be between 8 to 54%, but the FEV-P was not derived as the experimental site was non-responsive to increasing mineral P rate. Ashekuzzaman et al (2019a) provided a theoretical estimation of the FEV for the four types of Irish DPS from the total nutrient concentration (N, P, K), which showed a wide variation due to the considerable variation of DPS properties. In addition, the crop available fraction of N and P is still not well understood, which would play a vital role on the fertiliser value of DPS. The wastewater treatment process may have a significant effect on the plant available N and P. The ammonium-N (NH_4-N) concentration, which is easily plant available N, would decrease significantly with the use of lime (Libhaber and Orozco-Jaramillo, 2012), but may increase after an anaerobic digestion process (Mtshali et al., 2014). This effect on the plant availability of P is more complicated. Krogstad et al (2005) found that the P fertilising effect of sludge with biological purification without chemical additives and lime treatment could be comparable to mineral P fertiliser, whereas P fertiliser value of sludges precipitated by use of Fe and Al salts without liming treatment was very low. Kahiluoto et al (2015) found P was more available in sludge with a moderate Fe/P ratio (1.6), but had an adverse effect on the plant-availability of soil P with a surplus Fe coagulant (Fe/P of 9.8). Some studies have indicated that liming increases the plant-available P in sludge produced from the wastewater treated by Al and/or Fe salts (Bøen and Haraldsen, 2013; Krogstad et al., 2005; Montgomery et al., 2005). However, Kahiluoto et al (2015) found that P was not available to plants in the sludge hygienized with a high Ca/P ratio. Therefore, more agronomic trials are needed on the fertilising effect of N and P of different DPS relative to mineral FEV to optimise DPS utilisation.

2.5 Potential contaminants in DPS

A number of potentially harmful compounds may enter the milk processing chain through various routes and ultimately accumulate in DPS (Figure 2.2). Lactating animals are exposed to various chemicals, directly or indirectly, via the agricultural and veterinary practices on a farm (Fischer et al., 2011a). The active ingredient may be absorbed by animals, subsequently excrete into the milk, and eventually enter the waste stream through residual milk in the factory. In addition, some common contaminants such as dioxins and heavy metals are likely to be found in milk and dairy products, as they may enter and form incidentally during the production process (Fischer et al., 2011a). At present, there is limited information available on emerging contaminants in dairy processes. In this section, we list potential contaminants and their sources and fate in DPS.

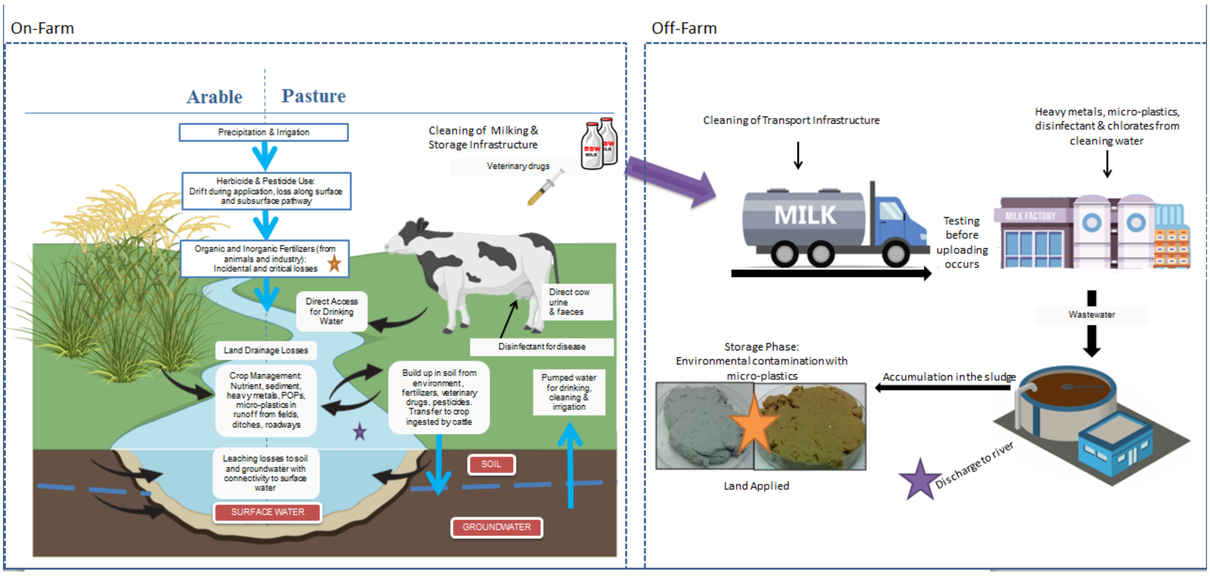

Figure 2.2 The sources and fates of emerging contaminants in DPS.

2.5.1 Antimicrobial drugs

Antibiotics, including the β-lactams (penicillins, cephalosporins), tetracyclines, macrolides, aminoglycosides, quinolones and polymyxins, are the most frequently and commonly used antimicrobial drugs in dairy cattle management (Fischer et al., 2011a). They are widely administered to treat, control and prevent spread of diseases of dairy cows such as mastitis, laminitis, respiratory diseases, and metritis, and to enhance animal growth and feed efficiency (International Dairy Federation, 1997). All the administered antibiotics could enter the milk and subsequently transfer to other dairy products to some extent, depending on their physicochemical properties and ability to intact with the fat and protein (Giraldo et al., 2017). Adetunji (2011) found streptomycin, penicillin and tetracycline residues in soft cheese and yoghurt. Rama et al. (2017) indicated that amoxicillin, penicillin G and cloxacillin were the most frequently detected residues in the raw milk collected from six different major regions of Kosovo. Sniegocki et al. (2015) observed that chloramphenicol can be easily transferred from raw milk to commercial butter, white cheese, sour cream and whey, as this antibiotic accumulates in dairy products with high fat content. The antibiotic residues in the dairy products may eventually enter the waste stream, but current wastewater treatment technologies are unable to remove traces of antibiotics from wastewater (Phoon et al., 2020). Once added to soil, antibiotics affect the structure and function of soil microbial communities and induce phytotoxic effects on plant growth (Jechalke et al., 2014). Current antibiotic wastewater technologies including advanced oxidation processes (AOP), advanced treatment (adsorption and membrane) and biological treatment, have advantages (AOP can destroy the chemical structure of pollutants) and disadvantages (the pollutants were degraded in AOP, but the toxicity remained) (Phoon et al., 2020). Hybrid technologies, involving several combinations of several technologies, are capable of removing antibiotics (Phoon et al., 2020).

2.5.2 Hormones

Endogenous hormones occur naturally in food of animal origin because animals can excrete steroid hormones. The amount excreted depends on age, state of health, diet, or pregnancy (Silva et al., 2012). Hormones are also used to promote growth, increase food production, medical treatment and improve reproductive performance, but the use of anabolic hormones in animal production is prohibited in the EU (EC, 1996; EC, 2003; IDF, 1997). Seventy-five percent of milk is produced predominantly by pregnant cows, which means that milk represents an important source of steroid hormones (Goyon et al., 2016). The natural hormone content of milk is typically between 40 and 500 μg/kg (IDF, 1997). During the processing in the dairy plants, the residual hormones will enter the effluent through residual milk. In a WWTP, some hormones are removed through sorption to TSS and degradation, followed by removal of the excess sludge (Silva et al., 2012), which means that hormones may accumulate in the DPS.

2.5.3 Pesticides

Pesticides, including insecticides, herbicides, rodenticides and fungicides, applied in agriculture, have been shown to transfer to dairy animal bodies through feed and fodder (Rather et al., 2017). In addition, to protect the animals against disease from mites, ticks and insects, some pesticides are directly sprayed to the animals when they are housed. Animals will absorb pesticides orally, cutaneously, or via inhalation in such closed environments (Fischer et al., 2011a). Currently, common pesticides, including organophosphate, pyrethoids and carbamates, can be used on both routes and lead to the bioaccumulation in the dairy products (Akhtar and Ahad, 2017). The pesticides used in the cropping system and their metabolites will be lost to the environment via volatilization, aerial drift, runoff to surface water bodies, and leaching into groundwater basins (Wang et al., 2019), which can accumulate in the dairy animals or directly compromise drinking water used in the dairy factory. The residues of organochlorines and their metabolites also need to be considered. Although banned in many countries since the 1970s, residues still can be found in the environment due to their persistence and prolonged efficacy (Fischer et al., 2011a, Akhtar and Ahad, 2017). There is a vast list of pesticides used currently or in the past in agriculture with various levels of persistence in the soil, bedrock and water phases (McManus et al., 2017). This could have implications for grazing animals especially on heavy drained soils where, for example, 2-methyl-4-chlorophenoxyacetic acid (MCPA), which has a high solubility and low adsorption to soil matrix, is used to clear vegetation and has been found to have a much longer residence time in anaerobic waterlogged conditions (Morton et al., 2020).

From the US Food and Drug Administration data, dichlorodiphenyltrichloroethane (DDT) and its metabolites dichlorodiphenyldichloroethylene (DDE) and dieldrin, are the most commonly detected pesticides in foodstuff, including baked goods, fruit, vegetables, meat, poultry and dairy products (Schafer and Kegley, 2002). The organochlorine pesticide, chlordane, has been found at a concentration of 1 ng/mL in raw milk samples (Fernandez-Alvarez et al., 2008). Golge et al. (2018) analysed 92 real dairy samples including raw milk, whole UHT (ultra-high-temperature) milk, Feta cheese and cream obtained from retail markets in Turkey, but none of the 167 pesticide residues were detected.

2.5.4 Disinfectants

Each procedure of the milk and dairy products process requires cleaning and disinfection to ensure removal of the bacteria and milk residues from all contact surfaces, including all processing equipment, transfer lines, tanks, trays, bins, blenders and conveyors (Cardador and Gallego, 2015). The most commonly used disinfectants are iodine-liberating agents, chlorine-containing substances, quaternary ammonium compounds, and hydrogen peroxide (Fischer et al., 2011a). A large amount of cleaning and disinfection agents enter dairy wastewater during the rinse-and-wash cycle of CIP system. Furthermore, using inadequately treated water to rinse and wash can be another source of contamination (McCarthy et al., 2018). Disinfectants are directly applied in the dairy wastewater to kill pathogens during wastewater treatment (Akhlaghi et al., 2018). The residual of disinfectants could be either in their original state or as disinfection by-products (DBPs). Iodine sanitizers, usually as iodophors, are widely used in teat and skin disinfectants, filling/packaging machines, culture processing equipment, drop hoses, and hand dipping stations (Hladik et al., 2016). Iodinated DBPs are considered to be one of the most toxic DBPs, but have been tested less frequently than chlorine DBPs (Postigo and Zonja, 2019). Hladik et al. (2016) found trihalomethanes (THMs), including iodinated THMs, in the dairy wastewater and surface waters that receive dairy effluents (either directly from the dairy or through a WWTP).

Sanitation of water and equipment with chlorine-containing substances such as chlorine gas (Cl_2), chlorine dioxide (ClO_2), chlorhexidine and hypochlorite (ClO^-), remains common practice due to chlorine's bactericidal and oxidative properties (McCarthy et al., 2018). Chlorine reacts with any natural organic matter present in milk to form chlorine DBPs (Cardador and Gallego, 2015). Cardador and Gallego (2015) tested 84 milk and dairy products samples and found that 17 of them contained haloacetic acids (HAAs), the major class of non-volatile DBPs. The HAAs found in commercial samples can be attributed to contamination within the industrial processes like the washing of packages and equipment.

2.5.5 Persistent organic pollutants (POPs)

There are thousands of persistent organic pollutants (POPs) widespread in the environment. POPs tend to accumulate in the food chain because of their lipophilicity and low biodegradability (Jones and Voogt, 1999). Since POPs occur ubiquitously, dairy animals are at danger from various sources of POPs, and these contaminants may transfer to the milk. In addition, some POPs such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins and furans, are common by-products or formed incidentally in industrial processes, and may subsequently enter the wastewater and sludge (Fischer et al., 2011b). PAHs are generally formed through a series of combustion processes occurring in industrial units. Boruszko (2017) detected 16 PAHs contents in three types of DPS and found 689 μg/kg dry matter (DM) in excess sludge, 95μg/kg in post-flotation sludge, and 497.7 μg/kg DM in a mixture of excess and flotation sludge, which are considerably lower than the maximum permissible content of PAHs in biosolids (6 mg/kg DM) defined by EC (EC, 2000). A survey on 239 raw milk samples in France found that the average polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and PCBs concentrations were 0.33 pg toxic equivalent (TEQ)/g fat and 0.57 pg TEQ/g fat, respectively (Durand et al., 2008). Mamontova et al. (2007) found PCBs residues in milk and obtained a good correlation between PCB concentrations in milk and soil. Furans can be formed from the dehydration of sugars and would be expected to be found in dairy products that have been heated. Heaven et al. (2014) found three analogues of furan in the milk sample.

2.5.6 Microplastics

Plastic particles with diameters ranging from 0.1μm to 5 mm are defined as "microplastics" and are a widespread anthropogenic pollutant in the environment with the extensive use of plastic (Phuong et al., 2016). Microplastics are mainly derived from synthetic fibres in clothing, industrial processes and personal care products, such as face cleaning soaps (Åström, 2016; Fendall and Sewell, 2009; Mahon et al., 2017). As an important food processing industry, the fate and sources of microplastics during the production process of dairy industry are largely unknown. The possible risks of milk contamination for microplastics may occur from cleaning equipment, the surrounding environment, as well as water supply conditions and inadequate handling of milk (Kutralam-Muniasamy et al., 2020). In addition, plastic-based packaging materials may lead to the microplastic contamination of milk. Kutralam-Muniasamy et al. (2020) collected 23 milk samples in Mexico and measured microplastics in the samples with an average of 6.5 ± 2.3 particles/L.

2.5.7 Nano particles

Nanotechnology, the designing and manufacturing of nano-scale (<100nm) materials with specific chemical and physical properties (Kaegi et al., 2011), has been widely used in such applications as medicines, alternative energy, catalysts, and consumer products (Wang et al., 2017). Nanoparticles (NPs) primarily include silver, gold, copper, copper oxide, zinc oxide, titanium dioxide, manganese oxide, carbon nanotubes and magnetic matter (Wang et al., 2017).

WWTPs are one of the most important pathways for NPs to enter the environment. The presence of NPs may have an effect on P removal and recovery (Chen et al., 2013).

2.6 STRUBIAS materials derived from DPS

Dairy factories produce large amount of DPS, which, on occasion, cannot be applied to land due to the limited nearby land bank for its application. This suitability may be driven by many factors such as soil type, crop type, weather conditions for trafficability, or farmer perception due to a lack of knowledge on crop and sample specific FEV. Local oversupply of DPS leads to environmental issues including nutrient runoff, leaching, methane emissions, odour, and the accumulation of certain substances in soil through application over many years (Gascó et al., 2018; Kwapinska et al., 2018). Incidental runoff losses of nutrients and carbon from land application of DPS may also pose a risk to surface water quality deterioration. A recent study showed that edge of field-losses of NH_4-N and carbon from three types of DPS application was highest for Fe-rich DPS, whereas Ca–P-rich DPS showed highest dissolved reactive P losses but lowest losses of NH_4-N and carbon (Ashekuzzaman et al., 2020). Therefore, in the long term, there is a need to find alternative technologies to recover energy and nutrients from DPS. STRUBIAS manufacturing technologies has attracted attention and can potentially add value to DPS. The potential use, current problems and knowledge gaps of STRUBIAS products are investigated in this section (Table 2.5).

Table 2.5 The potential of DPS and its by-products application and current knowledge gaps.

Products	**Potential Use**	**Current Problems**	**Current Scientific Knowledge Gaps**
Bio-chemically treated activated sludge "AC"	As a grassland and arable organic fertiliser	Farmers need more fertiliser value to optimise application and maximise yield responses, odour and local oversupply	Full nutrient and emerging contaminant content characterisation, N-P-K fertiliser value for a variety of crops and soil types, gaseous emissions and long-term agronomic trials absent.
Lime treated DAF sludge "DAF"	As a grassland and arable organic fertiliser	Farmers need more fertiliser value to optimise application and maximise yield responses, odour and local oversupply. Decomposes quickly leading to fungus problem	Full nutrient and emerging contaminant content characterisation, N-P-K fertiliser value for a variety of crops and soil types, gaseous emissions and long term agronomic trials absent.
Sludge Ash	Phosphorus resource.	High heavy metal content	Need technology to remove heavy metals. Alternative uses.
Biochar	Energy production, carbon sequestration, organic soil amendment, absorbent for heavy metals	The impacts on soil and crops, the heavy metal and organic contaminants, the cost of production and transportation	The properties of chars and the mechanism of interaction between chars and soil, long term environmental risk
Pyrochar	Carbon sequestration, organic soil amendment, absorbent		Very few studies on pyrochar and hydrochar. More data are needed. What are suitable amendment rates and how often? Fertiliser value, the technology to remove heavy metals from feedstocks (ash and hydrochar) and optimise the P recovery
Hydrochar	Energy production, carbon sequestration, organic soil amendment, absorbent, bio-refinery.		
Struvite	Phosphate fertiliser	The technology of struvite precipitation	More research is needed on the purity of struvite.

2.6.1 Struvite

Struvite (magnesium ammonium phosphat hexahydrate, $MgNH_4PO_4.6H_2O$) is a P mineral that can be precipitated from aqueous waste streams by increasing the pH of wastewater and maintaining a stoichiometric PO_4^{3-} to Mg^{2+} molar ratio (Hertzberger et al., 2020). Struvite precipitate is normally formed in WWTPs during the anaerobic digestion process when significant levels of Mg occur in the wastewater (Booker et al., 1999). Occasionally, large amounts of struvite may form and deposit on the walls of the digesters and connecting pipes, which results in downtime, loss of hydraulic capacity and increased maintaining costs (Booker et al., 1999). However, struvite precipitation is an effective P recovery method. The pilot and operational facilities that manufacture struvite are commonly installed at municipal WWTPs, but are not frequently installed at food processing plants (Huygens et al., 2018). Struvite is an excellent fertiliser because it has similar fertiliser efficiency to common mineral P fertilisers such as single super phosphate and triple superphosphate (Johnston and Richards, 2003). Compared with traditional fertilisers, struvite has a high P_2O_5 content, and is an excellent slow release fertiliser that does not "burn" roots when over applied (Xu et al., 2012). The fertilising effect of the struvite precipitate on maize was investigated in a pot trial and the results obtained show that struvite can be an effective source of fertiliser (Uysal and Kuru, 2015). Struvite precipitation from different wastes like dairy, urine, swine manure, semiconductor wastes, sludge, and reject water from sludge thickening and dewatering process is also practised (Li et al., 2019; Ren et al., 2015). However, the chemical compositions of waste-recovered struvite are not always consistent with pure struvite (Hall et al., 2020). Furthermore, metal impurities such as Al, Fe, Ca and small amount of heavy metals can also precipitate along with the struvite (Li et al., 2019). Dairy waste including wastewater, DPS and other STRUBIAS co-products show a significant potential for P recovery in the form of struvite. Uysal and Kuru (2015) detected high N, P and Mg contents in struvite precipitate produced from dairy industry wastewater, while heavy metal concentrations were below detection limits. However, if the dairy wastewater is rich in Ca, the struvite crystallization rate and product quality might be affected and may require additional steps (e.g. calcium removal or step-by-step precipitation) as a pre-treatment process (Li et al., 2019). Chelating agents like ethylenediaminetetraacetic acid (EDTA) addition, sodium carbonate addition and CO_2 stripping are the feasible technologies to remove Ca in wastewater to enhance the purity of the obtained struvite (Hu et al., 2020; Zhang et al., 2010). Becker et al. (2019) reclaimed both N and P from hydrochar-derived sewage sludge and its process liquid via struvite precipitation. An acid leaching step removed phosphate from the hydrochar, while the process liquid arising from hydrothermal carbonisation (HTC) was used as an NH_4 source for struvite precipitation. Xu et al. (2012) used an acid leaching method to extract P and produce struvite from sludge ash, which recovered more than 97% of P in sludge ashes.

To date, very few studies have investigated struvite precipitation from the dairy industry. The efficiency of P recovery and the precipitation technology needs to be further studied and optimised, as there are multiple factors that could potentially lead to inconsistency in the composition and speciation. In addition, research is needed to assess the toxicological compounds in the struvite because the contaminants in hydrochar and sludge ash might be simultaneously leached during P extraction.

2.6.2 Char-based materials

The term “char-based materials” is used here to replace ‘biochar’ in the STRUBIAS acronym, as they have different terms depending on the technology. Char-based materials obtained from the thermochemical conversion of biomass in an oxygen-depleted atmosphere are porous and carbonaceous, and are more stable and C-rich and less toxic than the feedstock (Atallah et al., 2020; Kambo and Dutta, 2015). Different thermochemical pre-treatment processes and conditions result in different final products. Pyrolysis is a prevailing thermal decomposition technology of OM (e.g. agricultural wastes, lignocellulosic biomass and sewage sludge) to convert biomass into valuable products like biochar, bio-oil and gas components at temperatures between 350 and 1000 °C in the absence of oxygen (Nanda et al., 2016; Ashekuzzaman et al., 2019b). Pyrolysed OM with a C content higher than 50% of DM are defined as biochar, otherwise, they are defined as pyrochar (EBC, 2012). HTC is, in contrast to pyrolysis, a wet conversion technique, degrading the OM content of sludge in the presence of water at a temperature range of 180-260 °C (Kambo and Dutta, 2015). Other than in pyrolysis, the HTC process does not require the drying of feedstock before and/or during the reaction (Malghani et al., 2013; Fakkaew et al., 2015). The HTC process produces a solid product, known as hydrochar, and a process liquid with high loads of small-chain organic acids, NH_4 and phosphate (Becker et al., 2019). It may therefore be more energetically efficient to convert wet biomass like DPS to hydrochar (Mau and Gross, 2018).

There are many functions of char-based materials including, but not limited to, energy production, agriculture, carbon sequestration, wastewater treatment and bio-refinery (Kambo and Dutta, 2015). The utility of a specific char-based material for any particular application depends on its inherent properties, which are mainly affected by their feedstock, pre-treatment method, and temperature (Amoah-Antwi et al., 2020). For energy production, hydrochar is a very suitable candidate as hydrochar shows considerable reduction in the ash content compared to that of raw feedstock and biochar produced via slow pyrolysis (Kambo and Dutta, 2015). In agriculture, the use of char-based material as a soil amendment is anticipated to improve chemical, physical and biological properties of soil and thereby crop productivity (Laird et al., 2010). Those rich in available nutrients and minerals and/or showing high water holding capacity could be better used as soil amendments to improve fertility (Graber et al., 2010). If char-based materials are used for C sequestration, it is necessary for them to have high environmental stability (Mašek et al., 2013). The stability of biochar in soil depends on several factors, especially the production method (Lehmann et al., 2009). Studies have rejected the potential of using hydrochar for carbon sequestration due to the low stability of hydrochar in soil (Berge et al., 2013; Eibisch et al., 2013). Biochar usually has a high specific surface area (SSA, >400 m^2/g) and more condensed polyaromatic structures, and hence is a good adsorbent for various contaminants (Amoah-Antwi et al., 2020; Kambo and Dutta, 2015). Hydrochar usually has very low SSA and porosity compared to biochar; however, due to the presence of oxygen-rich functional groups on its surface, the adsorption capacity of hydrochar is also high (Liu et al., 2010). The HTC process is promising in the field of pyrolysis of biomass for bioenergy production. The intermediate products includes 2,5-HMF, aldehydes (acetic, lactic, propenoic, levulinic, and formic acids), and other phenolic compounds generated during HTC can potentially be used for the manufacture of chemicals in the bio-refinery industry (Kambo and Dutta, 2015). DPS could be potential candidate for thermochemical treatment due to its low heavy metal content. Sadeghi et al. (2018) spread biochar derived from air-dried DPS over the surface of small-scale boxes filled with an erosion-prone soil and found that the biochar increased C, N, OM and C/N of the soil. In addition, they detected that biochar production significantly decreases the heavy metal, N, P and K contents, and increased the C and C/N ratio compared to raw dairy wastewater. Their study showed the potential of DPS-derived biochar to be an eco-friendly soil amendment and carbonaceous adsorbent. Ashekuzzaman et al. (2019b) studied pyrochars originating from two DPS types, i.e. activated sludge and DAF sludge, and used them as a carbonaceous adsorbent for P removal from wastewater. They found that the type, composition and the mineral composition (i.e. availability of Ca, Mg and Si) of DPS-derived pyrochar samples were associated with P removal process. Atallah et al. (2020) carried out batch HTC experiments using DAF sludge to investigate the effects of changing temperature, residence time and water-sludge ratio on the yield and quality of the hydrochar. They found that the production of hydrochar improved the characteristics of DPS, and an increase in reaction temperature, residence time and water-sludge ratio increased the hydrochar yield along with their energy and carbon content, and decreased the oxygen and volatile matter content.

Despite the benefits of char-based materials, there are several knowledge gaps with respect to the application of char-based materials derived from DPS. First of all, thermochemical treatments increase the risk of producing chars with other highly toxic compounds produced from high-temperature reactions such as PAHs, PCBs, dioxins, furans, and PCDD/Fs (Amoah-Antwi et al., 2020; Kambo and Dutta, 2015). Heavy metals present in the feedstock are most likely to remain and concentrate in the chars (Shackley et al., 2010). Therefore, careful analysis of feedstock and final products is necessary to avoid contamination in the soil. Second, char-based materials are complex, multi-functional materials that require improved mechanistic knowledge and understanding of its production, properties, impacts and interactions. The knowledge of char-based materials, especially hydrochar, derived from DPS is still in its early stages of development and all the aspects mentioned require additional research. Their benefits should be maximized through the mechanistic process understanding. Third, the cost of collecting of feedstocks, transportation, production and storage need to be properly assessed and managed.

2.6.3 Ashes

Ashes are characterized as fly ash or bottom ash, or a combination formed through the incineration of bio-based materials by oxidation (Huygens et al., 2018). They can be obtained from incineration plants which produce ash-based materials specifically for further agricultural use, or can be a production residue resulting from incineration of wastes or other production process (e.g. energy). Ash normally contains valuable plant macronutrients such as K, P, S, Ca and Mg (Brod et al., 2012; Haraldsen et al., 2011; Insam and Knapp, 2011), especially the amounts of P (13.7%-25.7% P_2O_5), which can be comparable to commercial superphosphate (Xu et al., 2012). However, the potential utilisation of ashes as fertiliser is limited, since it is also inevitably enriched in heavy metals (Franz, 2008; Herzel et al., 2016). Sludge ash could be a secondary feedstock in the production of marketable phosphate fertiliser. So far, there have been a number of studies on the technologies to extract and recover P from sewage sludge ash. Nakagawa and Ohta (2018) used alkaline leaching technology to recover P as calcium hydroxyapatite from sewage sludge ash. Acid solutions like H_2SO_4, HCl, HNO_3, and H_3PO_4 are usually used for ash leaching to extract P (Biswas et al., 2009; Tan and Largerkvist, 2011). Franz (2008) recovered P as fertiliser by adding lime water to precipitate calcium phosphates and other calcium compounds. Herzel et al. (2016) used a new thermochemical process for sewage sludge ash treatment, which transformed the phosphate-bearing mineral phases into plant available phosphates.

2.7 Conclusion and future research

Based on the EU's Farm to Fork Strategy, sustainable agriculture and organic farming will be encouraged in the future. DPS is recognised as a new organic fertiliser and a potential feedstock of STRUBIAS products. STRUBIAS products have potential commercial applications as both fertilisers (e.g. struvite), fertiliser components and soil amendments (e.g. chars). An important outcome of this review is that testing and publication of nutrient and metal data pertaining to DPS and DPS-derived STRUBIAS characteristics is not common. This is exasperated by the lack of testing and publication of data for other constituents such as heavy metals, pathogens, antimicrobial drugs, hormones, pesticides, disinfectants, POPs, microplastics and nano particles. These constituents, introduced during processing or treatment of the products, may be present at the land application stage. This is of particular concern for bioaccumulation in the soil and crops, with associated incidental losses in surface or near surface runoff to the aquatic environment. In addition the nutrient content and availability to plants differs across sludge and STRUBIAS product types due to many factors such as the type of dairy processing plant, wastewater treatment process and production technologies. Equally, the fertiliser equivalency value for both P and N is not known for all products and is not factored into application rates. This means that at farm scale neither agronomic nor environmental needs are being optimised. Future work should focus on these outcomes in long term field trials.

Summary

This chapter reviewed current knowledge of dairy processing waste including their nutrients profile, re-use pathways and potential challenges for these products in agriculture. The next chapter focuses on the characterisation of DPS and DPS-derived STRUBIAS products and a provides a method to determine their safe application to land.

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Chapter 3 An examination of maximum legal application rates of dairy processing and associated STRUBIAS fertilising products in agriculture.

This chapter presents the nutrient and metal composition of all main DPS and DPS-derived STRUBIAS product types and created a calculator that enables calculation of permissible application rates of these products in the context of EU soil and fertiliser regulations is developed. It has been published in the Journal of Environmental Management (Shi et al., 2022. An examination of maximum legal application rates of dairy processing and associated STRUBIAS fertilising products in agriculture, 301, 113880). Wenxuan Shi collected, analysed and extracted relevant information from scientific papers, and is the primary author of this article. Some of the DPS samples were collected by Wenxuan Shi on site and the rest of the DPS and STRUBIAS samples were collected prior to this study.

An examination of maximum legal application rates of dairy processing and associated STRUBIAS fertilising products in agriculture.

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Abstract

The dairy industry produces vast quantities of dairy processing sludge (DPS), which can be processed further to develop second generation products such as struvite, biochars and ashes (collectively known as STRUBIAS). These bio-based fertilisers have heterogeneous nutrient and metal contents, resulting in a range of possible application rates. To avoid nutrient losses to water or bioaccumulation of metals in soil or crops, it is important that rates applied to land are safe and adhere to the maximum legal application rates similar to inorganic fertilisers. This study collected and analysed nutrient and metal content of all major DPS (n = 84) and DPS-derived STRUBIAS products (n = 10), and created an application calculator in MS Excel™ to provide guidance on maximum legal application rates for ryegrass and spring wheat across plant available phosphorus (P) deficient soil to P-excess soil. The sample analysis showed that raw DPS and DPS-derived STRUBIAS have high P contents ranging from 10.1 to 122 g kg^{-1}. Nitrogen (N) in DPS was high, whereas N concentrations decreased in thermo-chemical STRUBIAS products (chars and ash) due to the high temperatures used in their formation. The heavy metal content of DPS and DPS-derived STRUBIAS was significantly lower than the EU imposed limits. Using the calculator, application rates of DPS and STRUBIAS materials (dry weight) ranged from 0 – 4.0 tonnes ha^{-1} y^{-1} for ryegrass and 0 – 4.5 tonnes ha^{-1} y^{-1} for spring wheat. The estimated heavy metal ingestion to soil annually by the application of the DPS and STRUBIAS products was lower than the EU guideline on soil metal accumulation. The calculator is adaptable for any bio-based fertiliser, soil and crop type, and future work should continue to characterise and incorporate new DPS and STRUBIAS products into the database presented in this paper. In addition, safe application rates pertaining to other regulated pollutants or emerging contaminants that may be identified in these products should be included. The fertiliser replacement value of these products, taken from long-term field studies, should be factored into application rates.

Keywords: agriculture; dairy processing waste; bio-based fertilisers; application calculator**.**

3.1 Introduction

The approach to sustainable nutrient use in agriculture is changing and there are ambitious new regulations incorporating “circular economy” objectives (EC, 2020a). In the European Union (EU) the “Farm to Fork Strategy” (EC, 2020a) aims to accelerate the transition from inorganic to organic sources of fertilisers within sustainable food and agriculture systems. One of the recommended practices is to encourage the recycling of critical nutrients (mainly nitrogen (N) and phosphorus (P)) from municipal, agricultural and industrial waste streams as fertilisers, which is important for the conservation of limited natural resources and the prevention of environmental pollution. As one of the largest agri-food sectors in Europe (Augère-Granier, 2018), the dairy industry consumes large volumes of water and generates wastewater (up to 10 L L^{-1} processed milk) that contains high concentrations of nutrients needed for crop growth (total nitrogen, TN: 14-830 mg L^{-1}; total phosphorus, TP: 9-280 mg L^{-1}; Erkan et al., 2018). The dairy waste stream, therefore, is a valuable resource for both N and P recovery.

Dairy processing sludge (DPS) is a settled solid-liquid by-product, rich in N and P, that is generated from dairy waste streams during wastewater treatment (Ashekuzzaman et al., 2019). Approximately 3.8 million tonnes are generated annually in the EU, which is equivalent to about 155 million tonnes of milk production (EC, 2020b). It is classified as a biosolid (Pankakoski et al., 2000), meaning that it may be applied to land as a fertiliser in most countries. For example, a recent report showed that 63% of the DPS produced in Ireland is applied to pasture and arable land and 13.6% is used for composting (Ryan and Walsh, 2016). DPS can be categorised based on the lime and metal salt addition during wastewater treatment, since P is frequently associated with calcium (Ca), aluminium (Al) and iron (Fe) in poorly soluble complexes (Brod et al., 2015). These elements are known to fix plant available P into unavailable forms in soil.

The valorisation of DPS into more stable (e.g. pelletized) fertiliser products is the most likely pathway to market. Raw DPS can be further processed into struvite, biochar and incineration ashes, collectively referred to as STRUBIAS (Huygens et al., 2018), which are categorised as secondary raw material-based fertilising products (EC, 2019). STRUBIAS materials have potential to become "component materials categories" (CMC) in the EU Fertilising Products Regulation (EC, 2019). This means that STRUBIAS materials can be used to produce fertilising materials with different intended functions, including inorganic and organic fertilisers, liming materials, growing media, soil improvers, plant biostimulants, and fertilising product blends (Huygens et al., 2018). To open the EU Single Market for these bio-based fertilisers, the new EU regulation will provide strict rules on safety, quality and labelling requirements for all types of fertilisers and will introduce new limit values for contaminants in fertilisers like cadmium (Cd) (EC, 2019). The dairy waste stream, including DPS and dairy wastewater, is a potential candidate for STRUBIAS materials production due to its high P concentration and low heavy metal content.

At present few studies that have examined the nutrient and metal profiles of DPS (which vary across processing plant, type, and seasonally) and DPS-derived STUBIAS products (Ashekuzzaman et al., 2019). As DPS is categorised as biosolids according to current practices in the EU (Pankakoski et al., 2000), its application to land is prohibited in some countries such as Belgium, Switzerland and Romania due to concerns of bioaccumulation of toxic metals and/or emerging contaminants in soil and crops (Milieu et al., 2013). There are also concerns that the processing of DPS into STRUBIAS products may introduce more metals, which could then cause problems for agricultural lands (Shi et al., 2021). Therefore, a thorough investigation and creation of a calculator that enables calculation of permissible application rates of these products in the context of EU soil and fertiliser regulations (Ulrich 2019) is needed but lacking, despite the fact that such work has been completed for other wastes spread on grasslands e.g. sewage sludge biosolids and bone meal on low P index soils (Lucid et al., 2013). In Ireland, land is used for crops, grazing, silage and forestry. Grassland (pasture, hay and silage) is the dominant crop (80% of utilisable land) (O'Donnell et al., 2021). The production of grass silage and arable crops like wheat to feed cattle is common (Velthof et al., 2014). Both of these dominant crops receive DPS and are therefore used in the present study.

The objectives of the current study were to: (1) collect, collate and present a comprehensive overview of nutrient and metal composition of the main DPS and DPS-derived novel STRUBIAS product types (2) calculate the maximum legal application rates for DPS and DPS-derived STRUBIAS for ryegrass and wheat, and (3) calculate the equivalent application rates of heavy metals.

3.2 Materials and methods

3.2.1 Sample Sources

A sample archive was collated consisting of 84 DPS and 10 DPS-derived STRUBIAS samples. Sixty-three DPS samples, collected from 2016 to 2018, originated from the study of Ashekuzzaman et al. (2019), and 21 DPS samples were collected in 2019 and 2020 for the current study. All DPS samples were collected using plastic containers with screw top lids from 12 dairy processing plants in Ireland. The DPS samples were categorised into three types, depending on the chemical added (Table 3.1): (1) activated sludge aluminum-precipitated (Al-DPS, n=54) (2) activated sludge iron-precipitated (Fe-DPS, n=9), and (3) lime-stabilised sludge calcium-precipitated (Ca-DPS, n=21). The 14 STRUBIAS products were categorised into three types (Table 3.2): struvite (n=3), chars (n=6), and ash (n=1).

Table 3.1 Dry matter, organic matter, pH and element concentration range in different types of DPS and comparison with regularity upper limit values for agricultural land application.

Sample Type	**DM**	**pH**	**OM**	**TC**	**TN**	**NH$_4$-N**	**TP**	**TK**	**Mg**	**S**	**Ca**	**Fe**	**Al**	**Cu**	**Ni**	**Pb**	**Cd**	**Zn**	**Hg**	**Cr**	**As**	**Mo**	**Reference**
	% of wt.		% of DM						g kg^{-1}										mg kg^{-1}				
Al-DPS (n=54)	12.5±3.2	7.1±0.5	68.4±8.1	32.6±5.9	57.6±8.8	3.8±1.8	34.7±11.1	7.4±3.9	3.6±1.7	5.5±1.6	41.8±20.0	1.4±1.0	34.5±16.6	2.4-34	<0.6-10.6	<2-4	<0.15-0.3	19-199.6	<0.1	2.5-19.6	<1.5	0.7-8.0	
Fe-DPS (n=21)	20.1±2.5	7.3±0.4	52.1±8.5	25.2±4.6	45.6±12.9	3.8±1.2	40.7±4.1	9.2±4.1	2.9±0.5	3.4±0.3	78.1±50.4	111.9±37.3	0.8±0.9	3.0-15.8	4.6-19.4	2.8-9.3	<0.15	92.6-180.6	<0.1	5.6-18.4	<1.5	<0.5-0.8	
Ca-DPS (n=9)	21.8±8.9	7.2±0.7	47.2±17.8	27.4±13.3	30.8±20.5	1.6±1.2	52.8±35.3	4.1±2.2	4.9±3.1	2.5±1.4	155.9±60.5	1.3±1.0	0.8±0.5	1.0-45.9	1.3-22.3	<2-9.6	<0.15-0.4	15.9-267.1	<0.1	3.2-17.2	<1.5	<0.5-22.5	
Regulations																							
EU limit														*1000-1750*	*300-400*	*750-1200*	*20-40*	*2500-4000*	*16-25*	-	-	-	*EEC, 1986*
Western Australia Grade C1														*100*	*60*	*150*	*3*	*200*	*1*	*100*	*20*	-	*Western Australia, 2012*
Western Australia Grade C2														*2500*	*270*	*420*	*20*	*2500*	*15*	*500*	*60*	-	
USA limit														*1500-4300*	*420*	*300-840*	*39-85*	*2800-7500*	*17-57*	-	*41-75*	*75*	*US EPA, 1993*

DM = dry matter, OM= organic matter, TC= total carbon, TN = total nitrogen, TP = total phosphorus, TK = total potassium

Al-DPS = aluminium-rich dairy processing sludge; Fe-DPS = iron-rich dairy processing sludge; Ca-DPS = calcium-rich dairy processing sludge.

Table 3.2 pH and element concentration range in DPS-derived STRUBIAS, comparison with regularity upper limit values for agricultural land application

Sample Type	pH	TC	TN	NH_4-N	TP	TK	Mg	Na	S	Ca	Fe	Al	Cu	Ni	Pb	Cd	Zn	Hg	Cr	As	Mo
		% of DM	g kg^{-1}										mg kg^{-1}								
Struvite (n=3)																					
MAP1		25.9	43.7	40.4	104.2	7.1	101.3	2.6	0.16	14.7	0.07	0.02	1.8	<0.6	<2	<0.15	30.1	<0.1	2.2	<1.5	<0.5
MAP2		38.8	29.4	15.4	80.2	7.5	62.2	8.8	0.46	34.5	0.17	0	0.21	<0.6	<2	<0.15	34.4	<0.1	2.8	<1.5	<0.5
CaMAP		31.6	11.2	0.33	47.0	6.5	18.8	31.7	0.62	66.9	0.39	0	0.38	<0.6	<2	<0.15	36.2	<0.1	3.3	<1.5	<0.5
Char (n=6)																					
PC1		28.4	19.4	0.046	52.3	14.7	8.0	9.3	7.1	97.0	4.1	33.8	44.7	13.8	16.4	0.29	269.6	<0.1	25.7	2.2	5.4
Al-PC2		29.4	52.8	0.12	108.5	20.3	11.0	4.8	8.1	69.6	1.3	47.5	14.4	3.0	<2	<0.15	337.8	<0.1	10.2	<1.5	4.4
Al-PC3		28.0	41.1	0.002	113.0	26.1	14.7	6.0	3.4	83.6	1.1	59.6	20.4	5.8	<2	<0.15	478.3	<0.1	13.5	<1.5	5.4
Fe-HC1	6.9	22.6	37.5	0.026	78.9	13.5	3.7	2.8	3.2	68.0	177.3	8.0	47.8	7.6	5.9	<0.15	186.1	<0.1	6.5	<1.5	<0.5
Fe-HC2	7.9	18.4	29.4	0.031	85.4	8.5	3.7	1.8	12.8	72.0	199.7	8.5	6.1	9.4	5.9	0.25	185.9	-	6.8	<1.5	<0.5
Fe-HC3	7.7	21.2	36.5	0.025	79.9	12.6	3.5	2.6	8.2	65.7	183.4	7.8	5.4	9.1	5.3	<0.15	171.7	-	6.8	<1.5	<0.5
Ash (n=1)																					
A1	9.3	0.90	1.1	0.092	99.3	26.7	17.0	20.5	11.9	227.5	7.5	82.1	92.7	27.4	32.6	0.68	482.4	<0.1	41.2	4.1	11.1
Regulation																					
EU[a]													*300*	*50*	*120*	*1.5*	*800*	*1*	-	*40*	-

DM = dry matter, TC= total carbon, TN = total nitrogen, TP = total phosphorus, TK = total potassium.

MAP1, MAP2 and CaMAP were produced from dairy processing wastewater by varying the pH, Ca:P, Mg:P and NH4+:P (Numviyimana et al., 2020).

PC1 was produced from a mixture of biological DPS and spruce wood chips at a pilot-scale facility (Kwapinska et al., 2019).

Al-PC2 and Al-PC3 were produced by an aluminium-rich dairy processing sludge at 450 °C and 700 °C for an hour respectively.

Fe-HC1, Fe-HC2 and Fe-HC3 were produced by an iron-rich dairy processing sludge through a HTC process with no additional water or with addition of 1% H2SO4 to achieve moisture contents of 85% and 90%, respectively.

A1 was produced by PC1 in a laboratory furnace at 650 ℃ for 3 h.

[a] EU (2019)

For struvite, three types of magnesium ammonium phosphate (MAP or struvite) were precipitated from dairy processing wastewater. The struvite precipitation was completed in a stirred batch reactor equipped with a 1 L beaker, water bath with temperature (22°C) regulation (PLWC 35S), and up-stirrer (CAT-100) with control settings for time (1 h) and stirring rate (60 rpm). Three types of struvites (MAP1, MAP2 and CaMAP; Table 3.2) were produced from dairy processing wastewater by varying the pH, Ca:P, Mg:P and NH_4^+:P (Numviyimana et al., 2020).

Six chars are included in this study. Three of them were produced by slow pyrolysis and are referred to as pyrochar. One (PC1; Table 3.2) was produced from a mixture of biological DPS and spruce wood chips at a pilot-scale facility (Kwapinska et al., 2019), while another two were produced using an Al-DPS at 450°C (Al-PC2) and 700°C (Al-PC3) for one hour (Hu et al., in preparation, 2021). The other three chars were produced through a hydrothermal carbonisation (HTC) process and are referred to as hydrochar (HC). These were produced using a raw Fe-DPS sample collected from a dairy processing plant in Ireland. The Fe-DPS sample was introduced into the reactor liner with no additional water (Fe-HC1; Table 3.2) or placed inside a reactor vessel with the addition of 1% H_2SO_4 to achieve moisture contents of 85% (Fe-HC2) and 90% (Fe-HC3), respectively. The time needed to reach the set point temperature (200°C) of the reaction was around 3 h for Fe-HC1, and around 26 min for Fe-HC2 and Fe-HC3. Once the set point was reached, the stirrer was initiated at 25 rpm and 36 rpm for 2 h. The solid HC separated from the liquid portion through filtration and dried in an oven at 105℃ for 24 h. PC1 was ashed in a laboratory furnace at 650℃ for 3 h (residence time) and cooled down to room temperature while still in the furnace. The generated ash (A1; Table 3.2) was grounded by mortar and pestle.

3.2.2 Sample analysis

All the raw DPS samples were stored in a cold room at 4℃ before analysis for dry matter (DM), organic matter (OM) and pH. The STRUBIAS samples were stored at room temperature and DPS were freeze dried at -55℃ for 48 h (ScanVac CoolSafe 55-9 Pro), before being pulverized in a mixer mill (Retsch MM200) with a vibrational frequency of 25 Hz for 1 min. The resulting powdered samples were stored in sample tubes at room temperature for nutrient, trace metal and other elemental compositional analysis.

The DM and OM were determined using standard gravimetric method 2540 G (APHA, 2005), where about 15-20 g of raw DPS was dried for about 24 h at 105℃ in an oven, followed by ignition of the dried residue at 550℃ in a muffle furnace for 1 h. The pH was determined in a 1:2.5 (w/v) ratio of fresh DPS to deionized water solution (making up to 25 ml) by a Jenway 3510 pH meter after 1 h of mixing at 20 rpm by an end-to-end shaker (Ashekuzzaman et al., 2019). The concentrations of nutrients (P, potassium (K), magnesium (Mg), sulphur (S), sodium (Na), and Ca) and metals (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), Al, Fe, cobalt (Co), molybdenum (Mo) and manganese (Mn)) were determined 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 (USEPA, 1996). Samples were also analysed for total carbon (TC) and TN using a high temperature combustion method (LECO TruSpec CN analyser). The mercury (Hg) analysis of two ash samples and three different samples, selected from the materials (Al-DPS, Fe-DPS, Ca-DPS, struvite, and chars), was conducted by inductively coupled plasma atomic fluorescence spectroscopy (ICP-AFS). The mineral fraction (total oxidised N and ammonium nitrogen (NH_4-N)) of total N was analysed colorimetrically in the 0.1M HCl-extracted filtered solution using an Aquakem 600 Discrete Analyser. For extraction, 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.

3.2.3 Calculation of maximum legal application rate ranges for DPS and STRUBIAS products

The application rates of organic fertilisers and STRUBIAS products to agricultural land take cognisance of the limiting annual loading rate for metals and the nutrient requirements of plants. In the EU, it is common that fertilisers are applied to land based on their P content (e.g. S.I. No. 610 of 2010 in Ireland), since applications based on the N requirement of a crop may result in excessive applications of P, which may cause nutrient losses to waters and, in the case of some biosolids, the build-up of heavy metals in the soil (Lucid et al., 2013). In Ireland, soil nutrient status is classified into index levels ranging from 1 to 4, depending on the quantity of the nutrient in the soil that is available to the crop (Table 3.3). The soil N index system is determined by the soil N supply status, while the plant available P is measured using Morgan's reagent (Teagasc, 2020). The application rate (in tonnes ha^{-1} y^{-1}) for the fertiliser products used was determined based on the P index level of the soil and the recommended N and P application rates for the target crop (such information is available in Ireland in the Teagasc Major and Micro Nutrient Advice for Productive Agricultural Crops green book; Teagasc, 2020), the legal limits of metals, the dry matter content of the fertiliser, and its nutrient and metal concentration. The optimal application rates of DPS and STRUBIAS products for two different crops, ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum* L.), were calculated using Microsoft Excel™ (Appendix B). Depending on the fertiliser application rates the annual equivalent loading rates of other elements including nutrients (N or P) and six EU regulated metals (Cd, Cu, Hg, Ni, Pb and Zn) are calculated (EEC, 1986).

Table 3.3 P Index system and annual maximum fertilisation rates of P for grassland and spring wheat

Soil P Index	Soil P ranges (Morgan's P mg/l)		P application rate (kg/ha)	
	Grassland crops	Other crops	Grassland	Spring wheat
1	0.0-3.0	0.0-3.0	40	45
2	3.1-5.0	3.1-6.0	30	35
3	5.1-8.0	6.1-10.0	20	25
4	>8.0	>10.0	0	0

Table 3.4 pH and element concentration range in the feedstock of DPS-derived STRUBIAS

Sample	**pH**	**TC**	**TN**	**NH$_4$-N**	**TP**	**TK**	**Mg**	**Na**	**S**	**Ca**	**Fe**	**Al**	**Cu**	**Ni**	**Pb**	**Cd**	**Zn**	**Hg**	**Cr**	**As**	**Mo**
Type		% of DM					g kg^{-1}										mg kg^{-1}				
Mixed bio-sludge[a]	-	35.9	57.6	-	36.7	7.2	0.88	4.4	8.5	31.3	1.5	9.1	31.4	12.5	23.5	1.57	194.4	-	12.5	3.14	4.70
Spruce wood[a]	-	50.8	2.1	-	0.008	0.23	0.06	0.05	0.02	0.52	0.01	0.01	0.73	0.32	0.89	0.08	8.00	0.08	0.16	-	-
Al-DPS[b]	7.7	36.2	71.6	4.6	39.7	10.5	4.7	2.2	8.1	31.9	0.7	19.2	7.82	2.54	<2	<0.15	199.6	<0.1	5.8	<1.5	2.1
Fe-DPS[c]	7.6	32.7	68.3	-	57.2	15.3	2.9	3.0	4.3	49.2	128.7	6.1	4.2	7.0	4.3	0.37	136.0	-	5.3	<1.5	<0.5
		%										mg kg^{-1}									
Wastewater[d]	4.4	3.07	0.14	364	444.8	1654.2	83.4	485.0	131.5	526.2	2.02	1.29	-	-	-	-	0.38	-	-	-	-

[a] A mixture of biological DPS and spruce wood chips in a 50/50 ratio by weight is feedstock of PC1 (Kwapinska et al., 2019). The mixed bio-sludge means the organic material, containing suspended solids and non-biodegradable pollutants such as heavy metals resulting from biological aerobic, anaerobic or anoxic waste water treatment processes

[b] An Al-DPS sample is the feedstock of Al-PC2 and Al-PC3.

[c] An Fe-DPS sample is the feedstock of Fe-HC1, Fe-HC2 and Fe-HC3.

[d] MAP1, MAP2 and CaMAP are from dairy processing wastewater.

3.3 Results and Discussion

3.3.1 Physicochemical composition

The DPS and STRUBIAS materials were characterised for nutrients and metal composition and compared to EU legislation on metal concentrations in Tables 3.1 and 3.2. The three types of DPS examined were rich in the major plant nutrients, but they were not significant sources of K due to the elutriating effect of wastewater treatment on soluble components, similar to other biosolids (Rigby et al., 2016). The N and NH_4-N-concentration was highest in the Al-DPS and lowest in the Ca-DPS. This may have been associated with lime addition, which causes losses of NH_3 and Ca-P precipitation (Ashekuzzaman et al., 2019). The concentrations of metals in the tested DPS samples were well below the EU regulatory guideline values (EEC, 1986). The concentrations of Cr, As and Mo are not currently regulated in the EU, but regulated elsewhere like western Australia and the USA (Western Australia, 2012; US EPA, 1993), and were well below the upper limits of 75, 75 and 500 mg kg^{-1}, respectively. In Western Australia, there are three contamination levels for each contaminant in biosolids: Grade C1 is for the highest quality of biosolids, Grade C2 is middle quality, and Grade C3 represents the lowest quality. The parameters of DPS were well under the Grade C1 values, except the Zn content of two Ca-DPS (209.7 and 267.1 mg kg^{-1}, respectively).

Struvite is the preferred form of P recovery for fertiliser by chemical precipitation, considering its provision of P and N for plant nutrition (Daneshgar et al., 2018). The high P content of dairy processing wastewater makes it attractive for P recycling (Numviyimana et al., 2020). Despite the potential to recover nutrients by struvite precipitation, the chemical composition of the final product can vary widely and is not always consistent with pure struvite (Ahmed et al., 2018). MAP1 is produced under optimum conditions enhancing struvite crystallization, MAP2 is formed in conditions of both P removal and struvite production, and CaMAP is obtained in conditions of maximum P recovery with high dose of Ca salts (Numviyimana et al., 2020). Therefore, both MAP1 and MAP2 had higher P and N concentrations than CaMAP, as Ca^{2+} can compete with the NH_4^+ and Mg^{2+}, reducing struvite yield. Typically, Ca^{2+} promotes the precipitation of calcium phosphate ($Ca_3(PO_4)_2$) and hydroxyapatite ($Ca_{10}(PO_4)_6OH)_2$), which are compounds of very low solubility (Bauer et al., 2007).

Slow pyrolysis reduced the contents of total C, N and S in the resultant chars, as during thermal treatment significant amounts of feedstock-bound elements are volatilised in the form of CO, CO_2, NH_3, hydrocarbon compounds HCN and H_2S (Lu et al., 2012; Tian et al., 2002; Zhang et al., 2017). Furthermore, the higher the pyrolysis temperature, the lower the C and N in the biochars (Al-DPS, Al-HC1 and Al-HC2 in Table 3.2). The C contents in the Al-PC1 and Al-PC2 declined by 18.8% and 22.7% with a pyrolysis temperature at 450°C and 700°C, respectively, compared to the TC contents in their feedstock (Al-DPS), while the biochar TN contents decreased by 26.2% and 42.6% with two different temperatures. The emission of different N groups, such as the conversion to NH_3 from protein N at low temperatures (400-440°C) and the conversion to HCN from pyridine at high temperatures (440-600°C), caused TN decline (Wei et al., 2015). The pyrochars had higher TP contents compared to their feedstocks (mixture of biological DPS and woodchip, and Al-DPS; Table 3.4) and the TP in the biochars increased with increasing pyrolysis temperature, which means pyrolysis concentrated the P components in the biochars (Yuan et al., 2011). The concentration of total K increased relative to temperature because of the inorganic association of K with DPS (Hossain et al., 2011). Total concentration of the other elements, including Na, Ca, Fe and Mg, increased after pyrolysis treatment.

HTC is a relatively new technology to treat biomass residuals and a solid value-added product, HC, is produced. In comparison to traditional pyrolysis technology, HTC requires wet feedstock and therefore the DPS does not need to be dried prior to or during the process, saving substantial amounts of energy (Langone and Basso, 2020). It is noteworthy that, no matter how the pH of the experiment changes, the pH values of the HCs were neutral, similar to other studies (Liu et al., 2020; Wang et al., 2017). The concentration of C and N in the HCs decreased compared to their feedstock (Fe-DPS). However, the losses of C and N were much lower than pyrolysis, because pyrolysis resulted in the emission of gases at higher concentrations than HTC (Mau and Gross, 2018). HTC is conducted at high pressures with a closed reactor and all gases generated during the process are only emitted once the treatment has concluded. In addition, NH_3 is not emitted as a gas due to the low pH of the aqueous phase (Mau et al., 2016). Therefore, N in the HC might be plant available, and volatilised C and N can be dissolved in HTC liquor. The S content in Fe-HC1 decreased compared with the feedstock DPS, while S in Fe-HC2 and Fe-HC3 increased due to H_2SO_4 addition during the HTC progress of Fe-HC2 and Fe-HC3. The results show that HTC increased the content of some nutrients including P, Mg, Ca, Fe and Al, while decreasing the content of Na and K. This means that the nutrients in the feedstock are not completely concentrated in the HC, as part of them were in the HTC liquor. There are still considerable uncertainties about both the composition of HTC process waters and their potential valorisation. It is recommended that technology developers measure the composition of process waters, especially with respect to possible application as fertiliser or for chemical recovery.

After the incineration of PC1 by oxidation, the contents of total C and N of ash significantly decreased, while all the other elements including nutrients and heavy metal concentration increased, which means they are concentrated in the ash.

Across three types of DPS-derived STRUBIAS products, the highest concentrations of Cu, Ni, Pb, Cd, Zn, Hg, and As were in ash and the lowest were in struvite. The total concentrations of Cu, Ni, Pb, Cd, Zn, Hg, and As in the chars and ash were higher than those in the feedstock DPS, but they were still under upper limits of the EU regulation for fertilisers (EU, 2019). It is likely that dissociation of organic compounds and some minerals, such as carbonates, caused by the pyrolysis temperature, contributed to an increase in heavy metal concentrations (Khanmohammadi et al., 2015).

3.3.2 Application rates based on nutrients

The high TP concentration in the DPS and STRUBIAS products examined in this study meant that maximum legal application rates for each soil P index were determined by the TP concentration of the material. The range of DPS and STRUBIAS application rates to ryegrass and spring wheat are shown in Figure 3.1. Based on the TP content of different types of materials, application rates varied from 0 to 4.0 tonnes ha^{-1} y^{-1} on grassland and from 0 to 4.5 tonnes ha^{-1} y^{-1} on spring wheat.

The application rates do not consider the plant-available N and P in the DPS and STRUBIAS, which will affect crop uptake of nutrients. In comparison with chemical fertilisers, organic fertilisers provide less readily available nutrients which can become slowly available as the growing season progress (Chen, 2006). Some bio-based products might have poor nutrient availability, despite their relatively high P content. For example, Ashekuzzaman et al. (2021a, b) assessed P and N availability of Al-, Fe-, and Ca-DPS for crop yield and uptake in comparison to reference mineral fertilisers over one year at field-scale experiment. Their results showed that P availability differs significantly between Al- and Ca-DPS, and that mineral P fertiliser was initially much more readily available for plant uptake than DPS, since Al-P and Ca-P are less soluble than mineral P fertiliser. With regards to N availability, Ashekuzzaman et al. (2021b) also found a wide range of N-fertiliser equivalency values (FEV) among different DPS types (8%-54%).

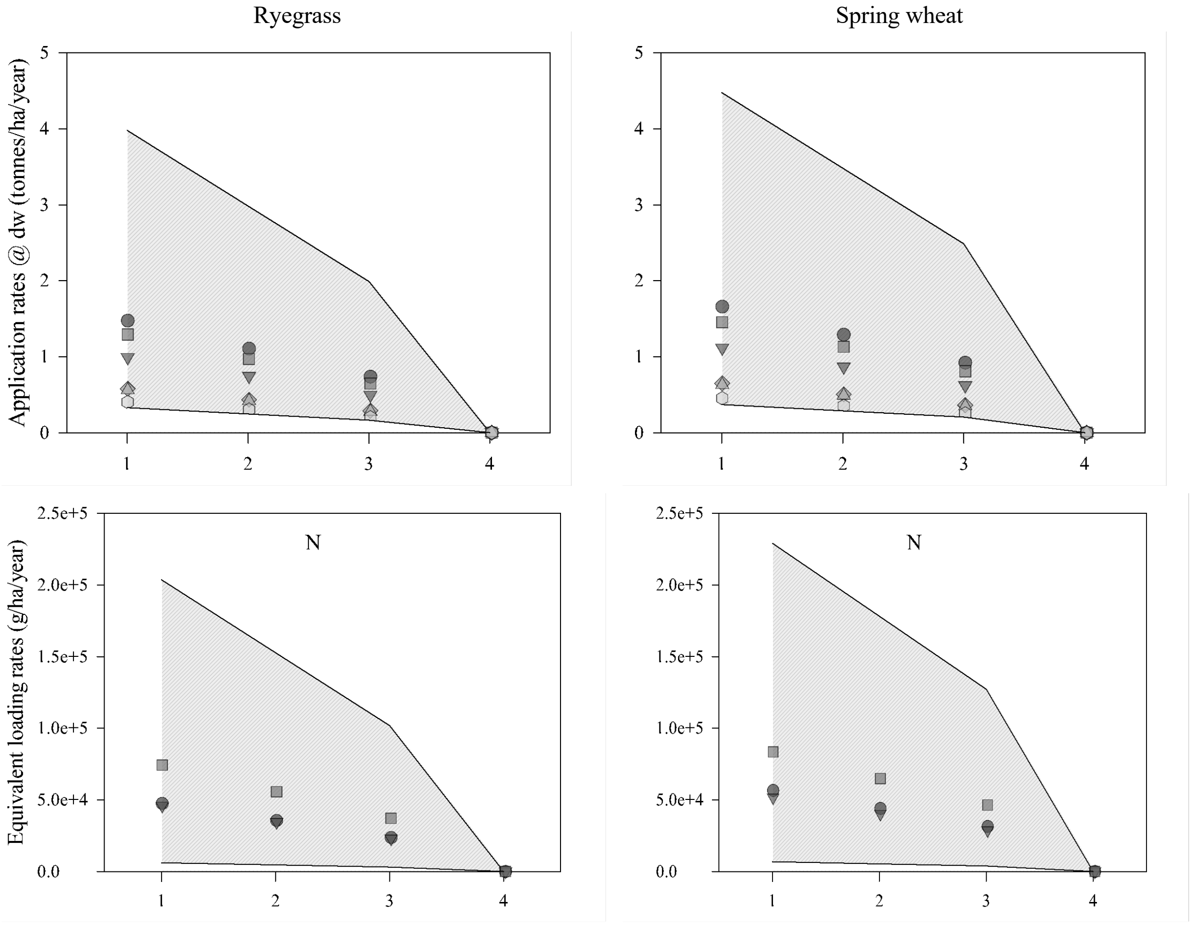
Numviyimana et al. (2020) evaluated nutrient availability to plant for three struvites, MAP1, MAP2 and CaMAP (also used in the current study; Table 3.2), in an *in*-vitro study, in which the nutrients released in 2% citric acid with pH 6 were measured over two hours. The results showed that although both MAP1 and MAP2 were characterized by higher P, Mg and N contents than CaMAP, MAP1 required a longer time to release N, P and Mg.

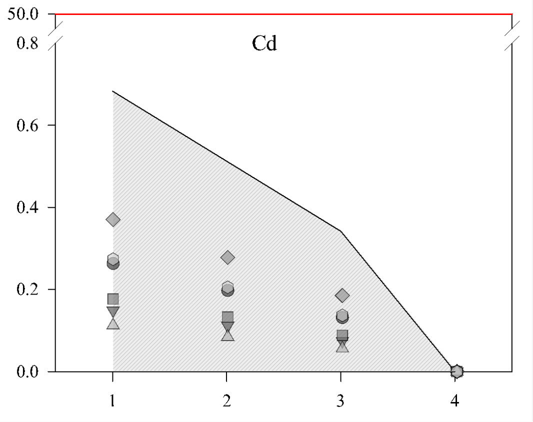
Biochar normally has low amounts of plant available N (Bridle and Pritchard, 2004). While losses of P during pyrolysis are negligible, P is converted into more stable, less available forms such as Mg or Ca minerals. Biochar, therefore, creates a more permanent nutrient pool for long-term nutrient uptake by crops (Fristak et al., 2018). In addition, NH_4-N and nitrate leaching reduce following biochar amendment (Yuan et al., 2016).

Ash from sludge incineration has higher P content (about 10%) than the original sludge before incineration (Lim and Kim, 2017; Liu et al., 2010). However, research shows that the bioavailability of P in the sludge ash is poor. The bioavailability of P can be estimated by the solubility of P in neutral ammonium citrate (P_{NAC}), mostly given as a fraction of the total P content (P_{NAC}-solubility) (Herzel et al., 2015). Krüger and Adam (2015) found that the mean P_{NAC}-solubility of sewage sludge ash in Germany is very low (31% of total P). The P species of sludge ash are controlled by the wastewater treatment before incineration, which means P is mainly associated with Al, Fe or Ca (Nanzer et al., 2014). Therefore, direct application of sludge ash as a fertiliser is very rare due to low bioavailability of P and significant amount of heavy metals (Jeon and Kim, 2017).

3.3.3 Estimation of equivalent loading rates of heavy metals

The EU sets average annual tolerance limits on heavy metal additions to soil over a 10-y period. These are (in g ha^{-1} y^{-1}) Cd: 50, Cr: 3500, Cu: 7500, Ni: 3000, Pb: 4000, Zn: 7500 and Hg: 100 (Fehily Timoney and Company 1999). The loading rates of six EU regulated heavy metals were determined based on the application rates of P in the DPS and STRUBIAS (Figure 3.1). All results show that application rates were low and considered safe in terms of bioaccumulation in soil and crops.

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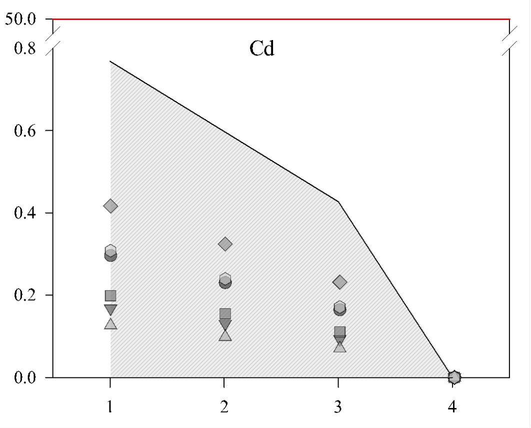
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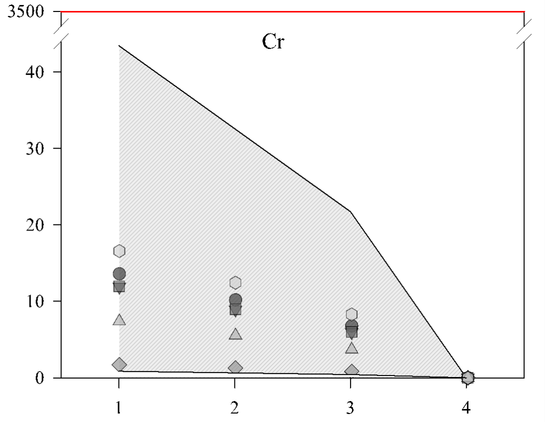
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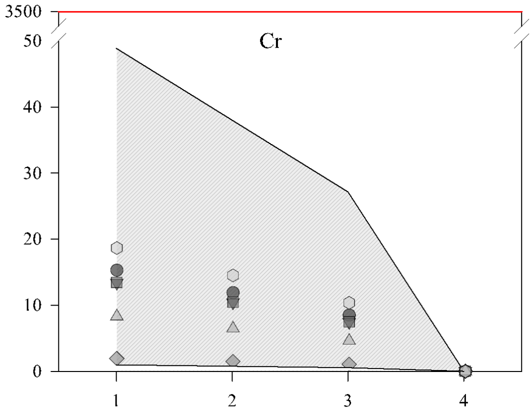
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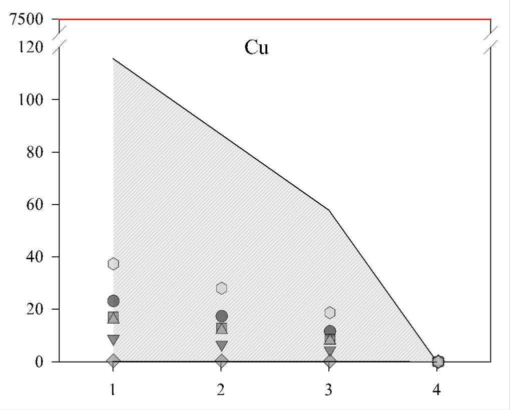
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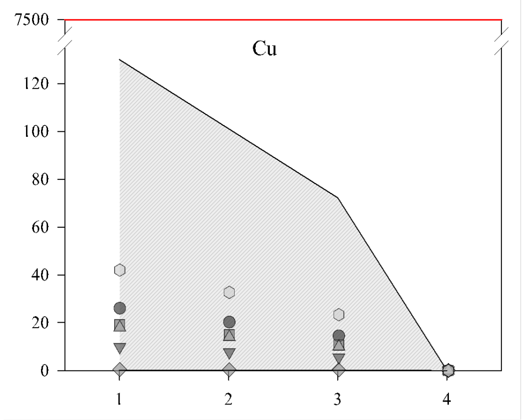
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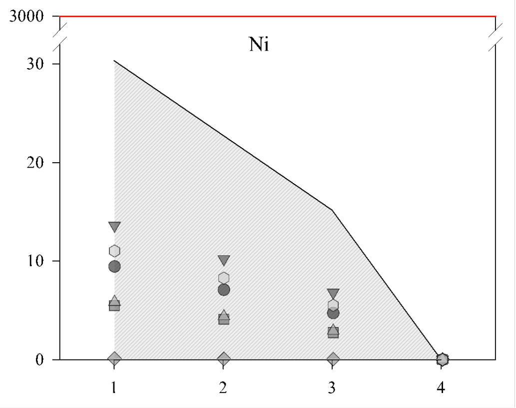
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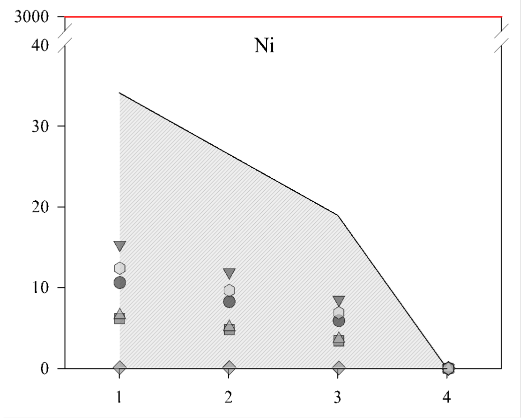
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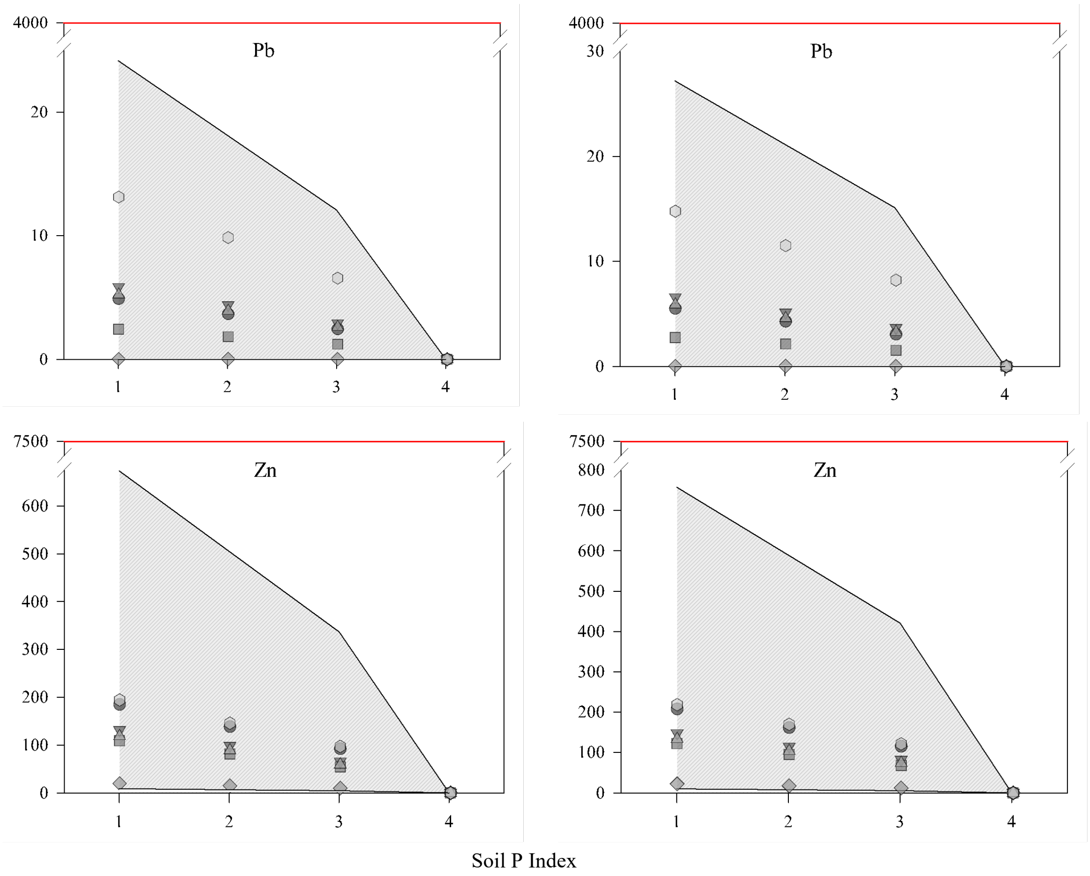

Figure 3.1 The maximum legal application rates of three types of DPS and three types of STRUBIAS fertilising products calculated based on the soil P index and the equivalent loading rates of N and regulated metals. [circle icon] = Ca-DPS; [upside-down triangle] = Fe-DPS; [square icon] = Al-DPS; [diamond icon] = struvite; [triangle] = char; [hexagon] = ash; [red line] = maximum heavy metal addition to the land. Shaded area represents the maxima and minima for the application rates, across all products, at each soil P index. Since Hg results were all below the limits of detection, it is not included in this figure.

Struvite has the lowest heavy metal content of all products included in Table 3.2. Many studies describe struvite as a slow-release fertiliser for agricultural applications, which is not highly soluble and therefore not readily lost along surface runoff pathways to waters (Cieślik and Konieczka, 2017; Yetilmezsoy et al., 2016). The production of struvite also reduces the mass of the original substrate through the loss of OM and moisture (Hall et al., 2020; Kim et al., 2009). Therefore, struvite precipitation from DPS offers a relatively effective and environmental-friendly way to recover excess nutrients from wastes.

Although themo-chemical treatments including pyrolysis, HTC and incineration, increased heavy metal concentration, most of the heavy metals existed in the oxidisable and residual forms, especially when pyrolysed at 600°C, resulting in a significant reduction in their bioavailability, leading to a very low environmental risk of chars and ash (Jin et al., 2016). However, if ash were directly applied to land, further processing to remove contaminants would still be needed.

3.3.4 Future Research Needs

Future research should focus on establishing the N-FEV and P-FEV of DPS and DPS-derived STRUBIAS products using pot and field trials. For example, the calculated application rates in this study do not consider the N and P availability of these products, which are more indicative of their performance as fertiliser replacements. Completion and incorporation of such research into the calculator for all DPS and STRUBIAS product and crop types would lead to more accurate incorporation of bio-based fertilisers into nutrient management planning. In addition, the application rates used in this study are regulated by guidance in Ireland, based on fixed nutrient application norms. Models that predict future P yields should represent a balance between P input and outputs in the field, which would lead to more efficient DPS and STRUBIAS application. Such a model has been completed for manure applications to both grassland and arable lands (Mollenhorst et al., 2020) leading to decreased P losses in waters where applied. The evolution of wastewater treatment techniques employed at dairy processing sites endeavours to follow advances in the treatment of human wastewater. From an economic perspective, there is a need to move away from dosing P-rich waste streams with metal salts towards biological P removal (Slavov, 2017). Such treatment will replace the need for metal flocculants to remove P, but will inevitably produce new sludge streams that will need to be characterised in terms of their FEV, nutrient and metal content.

Heavy metal and other emerging contaminants, present in some DPS or introduced due to the production of STRUBIAS products, need further review and characterisation. Indeed, the bioaccumulation of contaminants in soil and crops associated with land application of bio-based fertilisers needs investigation using long-term field trials since the accumulation of contaminants in soil, following repeated applications of these products, may be problematic. The calculator created in this study should be developed into an online or phone application to guide growers, contractors, farmers and processing plant operators, as part of on-going nutrient management planning.

3.4 Conclusions

A total of 84 DPS and 14 DPS-derived STRUBIAS products were examined for their safe agricultural land application to comply with regulatory requirement for application rates and soil metal contamination from bio-based fertiliser application. All products tested had high P content. Nitrogen in DPS was high, but N concentrations were low in the thermo-chemical STRUBIAS products. The heavy metal content of DPS and DPS-derived STRUBIAS tested were all lower than EU imposed limits and presented no problems regarding application rates. The calculated DPS and DPS-derived STRUBIAS maximum legal application rates, based on nutrients for ryegrass and wheat, were 0-4.0 tonnes ha^{-1} y^{-1} and 0-4.5 tonnes ha^{-1} y^{-1}, respectively. Future research should incorporate the FEV of DPS and STRUBIAS products into nutrient management planning. New wastewater treatment processes will lead to new DPS and STRUBIAS products, which will require analysis in long-term field trials.

Summary

This chapter presented the nutrient and metal profile of DPS and DPS-derived STRUBIAS products and developed a calculator for safe application rates estimation. The next chapter will examine the FEV of DPS and DPS-derived biochar, and how application rates and calculation methods of FEV will affect the results.

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Chapter 4 Mineral fertiliser equivalent value of dairy processing sludge and derived biochar using ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum*)

This chapter presents a pot study that investigated N- and P- MFE of two types of DPS and one DPS derived biochar to grow ryegrass and spring wheat. It has been published in the Journal of Environmental Management (Shi et al., 2022. Mineral fertiliser equivalent value of dairy processing sludge and derived biochar using ryegrass (*Lolium perenne L.*) and spring wheat (*Triticum aestivum*), 321, 116012). Wenxuan Shi developed the experiment design, set up the pot trial, retrieved samples, and analysed all samples derived from it. She is the primary author of this 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 (ryegrass ~50% and 70% for Al-DPS and Ca-DPS) with other calculation methods producing all similar results (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.

Keywords: agriculture; agronomy, bioeconomy, circular economy, dairy processing waste

4.1 Introduction

The global and European bioeconomy face multiple challenges, one of which is to choose safe alternatives to chemical fertiliser that can grow crops (EU, 2016). 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 (Figure 4.1), 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. 4.1 and 4.2).

$$\text{N-MFE (\%)} = \frac{EQ_{mineral\,N\,fertiliser\,rate}}{N_{applied}} \times 100 \tag{4.1}$$

$$\text{P-MFE (\%)} = \frac{EQ_{mineral\,P\,fertiliser\,rate}}{P_{applied}} \times 100 \tag{4.2}$$

Where $EQ_{\text{mineral N or P fertiliser rate}}$ 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). $EQ_{\text{mineral N or P fertiliser rate}}$ is determined using the regression between mineral fertiliser application rates (kg ha^{-1}) and crop response (N or P uptake or yield).

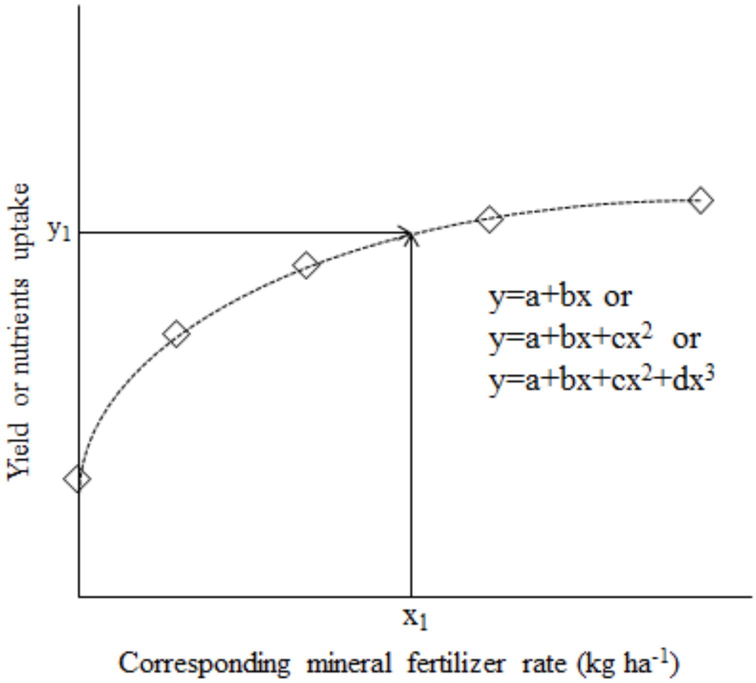

Figure 4.1 Illustration of the calculation of MFE by response curve. a is the intercept (crop yield or nutrients uptake at 0 kg ha^{-1} of mineral fertiliser); b, c and d are the linear, quadratic and cubic coefficients, respectively.

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 pots (N $uptake_{Control}$ or P $uptake_{Control}$) (Murphy et al., 2013) (Eqn. 4.3 and 4.4). 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 Eqn. 4.5 and 4.6.

$$ANR(\%) = \frac{N\ uptake_{\ Treatment} - N\ uptake_{Control}}{Total\ N\ applied_{Treatment}} \tag{4.3}$$

$$APR(\%) = \frac{P\ uptake_{\ Treatment} - P\ uptake_{Control}}{Total\ P\ applied_{Treatment}} \tag{4.4}$$

$$\text{N-MFE (\%)} = \frac{ANR_{Treatment}}{ANR_{Reference}} \times 100 \tag{4.5}$$

$$\text{P-MFE (\%)} = \frac{APR_{Treatment}}{APR_{Reference}} \times 100 \tag{4.6}$$

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.

4.2 Materials and methods

4.2.1 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 oxidised N and ammonium nitrogen (NH_4-N)) of total N was analysed colorimetrically in a 0.1M HCl-extracted filtered solution using a 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.

4.2.2 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 oxidised 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 a 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.

4.2.3 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 4.1). 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 (Figure 4.2). 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.

Table 4.1 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

Figure 4.2 Glasshouse pot trial with ryegrass and spring wheat.

Calcium ammonium nitrate (CAN) and super phosphate (SP) were used as the study reference (Eqns. 4.5 and 4.6) 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) (Table 4.2 and 4.3). 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 (Table 4.2 and 4.3). 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% to 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).

Table 4.2 Ryegrass pot design for N-MFE and P-MFE experiment.

Treatment	Product amount						
	CAN[1] (kg N ha^{-1})	SP[1] (kg P ha^{-1})	MOP[1] (kg K ha^{-1})	SOP[1] (kg S ha^{-1})	Al-DPS[2]	Ca-DPS[2]	biochar (kg P ha^{-1})
Control	-	-	-	-	-	-	-
			N trial				
CAN	0	60	160	20	-	-	-
CAN	20	60	160	20	-	-	-
CAN	60	60	160	20	-	-	-
CAN	100	60	160	20	-	-	-
CAN	125	60	160	20	-	-	-
CAN	160	60	160	20	-	-	-
Al-DPS	-	60	160	20	125	-	-
Al-DPS	-	60	160	20	160	-	-
Ca-DPS	-	60	160	20	-	125	-
Ca-DPS	-	60	160	20	-	160	-
			P trial				
SP	150	0	160	20	-	-	-
SP	150	10	160	20	-	-	-
SP	150	30	160	20	-	-	-
SP	150	40	160	20	-	-	-
SP	150	80	160	20	-	-	-
SP	150	100	160	20	-	-	-
Al-DPS	150	-	160	20	40	-	-
Al-DPS	150	-	160	20	80	-	-
Ca-DPS	150	-	160	20	-	40	-
Ca-DPS	150	-	160	20	-	80	-
Biochar	150	-	160	20	-	-	40
Biochar	150	-	160	20	-	-	80

[1] CAN=calcium ammonium nitrate, SP=super phosphate (SP), MOP=potassium chloride, SOP=sulphate of potash

[2] Unit of Al-DPS and Ca-DPS is kg N ha^{-1} for N trial and kg P ha^{-1} for P trial.

Table 4.3 Spring wheat pot design for N-MFE and P-MFE experiment.

Treatment	Product amount						
	CAN[1] (kg N ha^{-1})	SP[1] (kg P ha^{-1})	MOP[1] (kg K ha^{-1})	SOP[1] (kg S ha^{-1})	Al-DPS[2]	Ca-DPS[2]	Biochar (kg P ha^{-1})
Control	-	-	-	-	-	-	-
N trial							
CAN	0	60	130	20	-	-	-
CAN	50	60	130	20	-	-	-
CAN	100	60	130	20	-	-	-
CAN	160	60	130	20	-	-	-
CAN	200	60	130	20	-	-	-
CAN	240	60	130	20	-	-	-
Al-DPS	-	60	130	20	160	-	-
Al-DPS	-	60	130	20	240	-	-
Ca-DPS	-	60	130	20	-	160	-
Ca-DPS	-	60	130	20	-	240	-
P trial							
SP	200	0	130	20	-	-	-
SP	200	10	130	20	-	-	-
SP	200	20	130	20	-	-	-
SP	200	50	130	20	-	-	-
SP	200	80	130	20	-	-	-
SP	200	100	130	20	-	-	-
Al-DPS	200	-	130	20	50	-	-
Al-DPS	200	-	130	20	80	-	-
Ca-DPS	200	-	130	20	-	50	-
Ca-DPS	200	-	130	20	-	80	-
Biochar	200	-	130	20	-	-	50
Biochar	200	-	130	20	-	-	80

[1] CAN=calcium ammonium nitrate, SP=super phosphate (SP), MOP=potassium chloride, SOP=sulphate of potash

[2] Unit of Al-DPS and Ca-DPS is kg N ha^{-1}for N trial and kg P ha^{-1}for P trial.

4.2.3.1 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.

4.2.3.2 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.

4.3 Results & Discussion

4.3.1 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 4.4. 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).

Table 4.4 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

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 4.4), which may have impacted the absorption and utilisation of P and Mg by crops (Staugaitis and Rutkauskiene, 2012; Nest et al., 2021).

4.3.2 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 (Figure 4.3 and 4.4). The DPS treatments produced significantly higher cumulative yields of ryegrass DM than the study control (no N treatment) (Table 4.5). Application rates of Al-DPS significantly impacted the cumulative yield of the ryegrass, but there was no difference in cumulative yield at either application rate for the Ca-DPS (Table 4.5). 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 4.6).

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 4.5). 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 4.6).

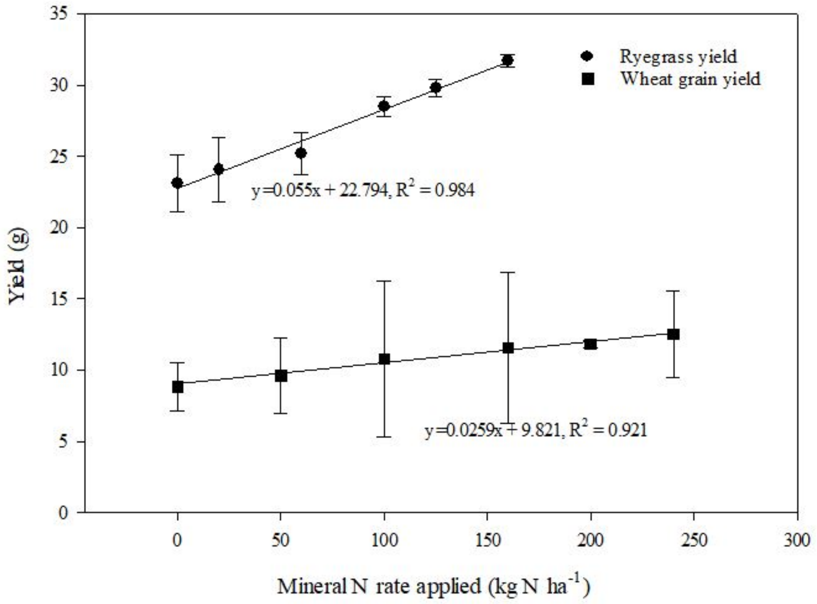

Figure 4.3 Response curve between ryegrass yield, spring wheat grain yield and N application rate.

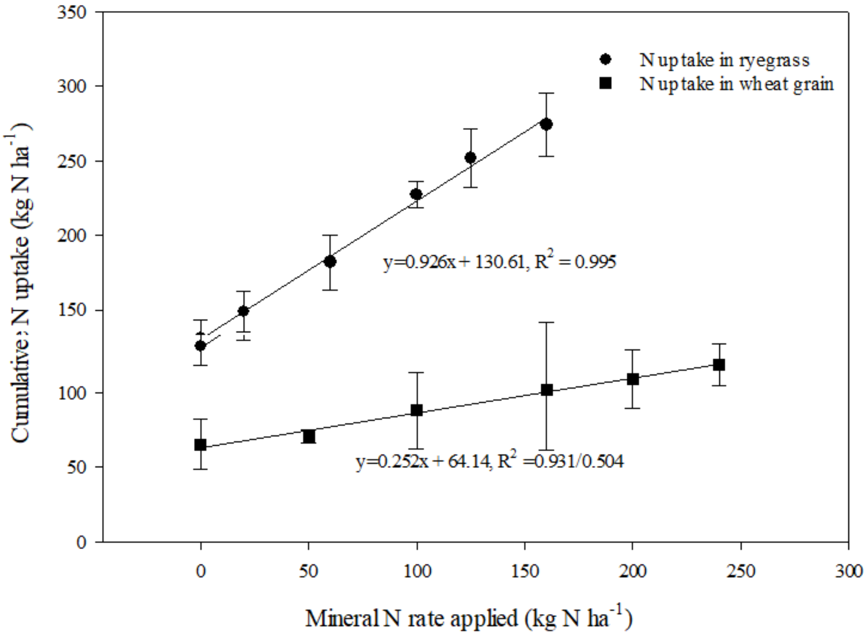

Figure 4.4 Response curve between N uptake in ryegrass, spring wheat grain and N fertiliser rate.

Table 4.5 Effect of treatment and N rate on ryegrass (*Lolium perenne* L.) dry matter yield and N uptake over the course of the N-MFE experiment across four harvests (11/08/20, 15/09/20, 02/11/20, and 04/01/21) over 6 months.

Treatment*	N rate	Harvest**									
		1	2	3	4	**cumulative**	1	2	3	4	**cumulative**
	kg ha^{-1}	Yield (g)					N uptake (kg N ha^{-1})				
CAN	0	8.7^{cde} (1.3)	6.9^{d} (0.5)	5.4^{c} (0.5)	2.1^{d} (0.3)	**23.1^{e} (2.0)**	61.0^{e} (11.3)	34.6^{f} (0.8)	25.4^{b} (0.6)	10.0^{d} (1.3)	**131.0^{f} (12.3)**
CAN	20	9.3^{bcd} (0.8)	6.9^{d} (0.7)	5.5^{c} (0.6)	2.3^{d} (0.3)	**24.1^{de} (2.3)**	74.1^{d} (10.0)	38.6^{ef} (1.4)	25.0^{b} (0.9)	11.2^{d} (1.9)	**148.8^{ef} (13.7)**
CAN	60	9.9^{bcd} (0.7)	7.6^{cd} (0.6)	5.6^{c} (0.3)	2.1^{d} (0.5)	**25.2^{de} (1.5)**	104.2^{c} (14.0)	42.2^{de} (2.2)	25.4^{b} (0.7)	10.0^{d} (1.9)	**181.8^{f} (18.5)**
CAN	100	10.3^{abc} (1.3)	9.4^{ab} (1.0)	6.2^{bc} (0.2)	2.6^{cd} (0.2)	**28.5^{b} (0.7)**	133.5^{b} (11.6)	52.1^{ab} (3.1)	28.4^{b} (1.7)	13.2^{bcd} (1.4)	**227.2^{b} (9.1)**
CAN	125	11.1^{ab} (1.5)	10.0^{a} (1.0)	6.5^{b} (0.2)	2.2^{d} (0.5)	**29.8^{ab} (0.6)**	159.3^{a} (20.9)	52.6^{ab} (3.3)	28.9^{b} (2.4)	10.7^{d} (2.5)	**251.5^{ab} (19.6)**
CAN	160	12.4^{a} (0.6)	10.3^{a} (0.4)	6.2^{bc} (0.3)	2.7^{cd} (0.1)	**31.7^{a} (0.4)**	174.5^{a} (14.3)	56.4^{a} (6.3)	29.6^{b} (1.3)	13.4^{bcd} (1.1)	**274.0^{a} (21.3)**
Al-DPS	125	9.1^{bcd} (1.1)	8.0^{cd} (0.6)	6.5^{b} (0.7)	2.5^{cd} (0.4)	**26.1^{cd} (1.2)**	70.2^{d} (10.6)	45.7^{cd} (3.6)	29.6^{b} (0.2)	12.9^{cd} (1.7)	**158.4^{de} (12.8)**
Al-DPS	160	10.0^{bcd} (1.2)	8.4^{bc} (0.2)	6.9^{b} (0.7)	3.3^{bc} (0.3)	**28.6^{b} (0.3)**	84.1^{cd} (9.8)	51.4^{ab} (3.1)	35.9^{b} (2.4)	16.8^{b} (0.6)	**188.1^{c} (14.0)**
Ca-DPS	125	7.9^{de} (0.8)	8.0^{cd} (1.0)	8.5^{a} (0.7)	3.7^{b} (0.7)	**28.1^{bc} (1.9)**	53.8^{e} (6.8)	47.0^{bcd} (2.3)	33.5^{b} (2.3)	16.0^{bc} (3.9)	**150.3^{ef} (9.6)**
Ca-DPS	160	6.8^{e} (0.2)	8.0^{cd} (0.5)	9.1^{a} (0.3)	4.5^{a} (0.6)	**28.3^{bc} (0.2)**	53.6^{e} (2.5)	51.2^{abc} (4.0)	49.3^{a} (21.1)	20.9^{a} (3.3)	**175.1^{cde} (20.6)**

[*] CAN: calcium ammonium nitrate; Al-DPS: aluminium rich activated sludge; Ca-DPS: calcium rich lime treated activated sludge.

[**] 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 ($n = 3$).

Table 4.6 Effect of treatment and N rate on spring wheat (*Triticum aestivum*) dry matter yield and N uptake over the course of the N-MFE experiment.

Treatment*	N rate	Harvest**			
		Chaff	Grain	Chaff	Grain
	kg ha^{-1}	Yield (g)		N uptake (kg N ha^{-1})	
CAN	0	12.6^{b} (4.5)	10.4^{a} (3.0)	25.8^{c} (10.5)	71.5^{c} (16.0)
CAN	50	13.1^{b} (0.8)	10.4^{a} (2.3)	27.2^{c} (2.9)	70.6^{c} (4.2)
CAN	100	16.2^{ab} (4.3)	12.9^{a} (5.9)	48.2^{bc} (2.0)	88.1^{bc} (25.8)
CAN	160	18.3^{ab} (5.4)	13.1^{a} (6.5)	49.1^{bc} (19.4)	101.7^{abc} (40.0)
CAN	200	20.8^{a} (4.7)	14.8^{a} (4.5)	63.5^{ab} (27.1)	109.0^{ab} (19.7)
CAN	240	19.4^{a} (4.3)	14.6^{a} (4.2)	92.8^{a} (13.1)	132.8^{a} (26.5)
Al-DPS	160	17.5^{ab} (1.1)	12.8^{a} (3.2)	34.9^{bc} (3.5)	107.0^{ab} (19.8)
Al-DPS	240	20.7^{a} (2.5)	15.1^{a} (1.7)	48.1^{bc} (7.3)	110.4^{ab} (16.9)
Ca-DPS	160	17.1^{ab} (0.3)	15.8^{a} (2.1)	34.1^{bc} (8.7)	100.8^{abc} (5.4)
Ca-DPS	240	17.2^{ab} (4.2)	13.4^{a} (2.8)	32.1^{bc} (9.5)	98.3^{abc} (4.3)

[*] CAN: calcium ammonium nitrate; Al-DPS: aluminium rich activated sludge; Ca-DPS: calcium rich lime treated activated sludge.

[**] 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 ($n = 3$).

Table 4.7 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. 4.1**	**N-MFE from N uptake response curve Eqn. 4.1**	**ANR Eqn. 4.3**	**N-MFE from Eqn. 4.5**
	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. 4.2**	**P-MFE from P uptake response curve Eqn. 4.2**	**APR Eqn. 4.4**	**P-MFE from Eqn. 4.6**
	kg ha^{-1}	**%[1]**	**%**	**%**	**%**
		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

[1] Crop yield is unresponsive to P application.

Depending on the method of calculation (ANR, N-MFE based on DM yield or N uptake rate), there were large differences in equivalencies (Table 4.7). The N-MFE based on DM yield (ranging from 47.6% to 77.4% for ryegrass and 57.3% to 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% to 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).

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 mineralisable 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.

4.3.3 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 (Figure 4.5). 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 4.8). 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 chaff and grain yields of the control and all treatments (Table 4.9). 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).

Table 4.8 Effect of treatment and P rate on the grass dry matter yield and P uptake over the course of the P-MFE experiment across 4 harvests (11/08/20, 15/09/20, 02/11/20, and 04/01/21) over 6 months.

Treatment[*]	P rate	Harvest[**]									
		1	2	3	4	**cumulative**	1	2	3	4	**cumulative**
	kg ha^{-1}	Yield (g)					P uptake (kg P ha^{-1})				
SP	0	11.6^{a} (0.6)	13.0^{a} (1.6)	8.3^{c} (1.4)	4.1^{c} (1.3)	**37.0^{a} (4.4)**	10.5^{de} (0.7)	12.8^{ef} (1.7)	11.2^{b} (1.1)	3.1^{c} (0.6)	**37.6^{e} (1.2)**
SP	10	11.1^{ab} (0.2)	14.2^{a} (0.2)	9.6^{abc} (0.8)	4.7^{c} (0.6)	**39.6^{a} (1.5)**	11.1^{cd} (0.6)	13.0^{ef} (1.3)	11.8^{ab} (1.3)	3.7^{c} (0.2)	**39.6^{de} (2.8)**
SP	30	12.3^{a} (1.2)	12.7^{ab} (1.4)	8.5^{c} (1.1)	4.2^{c} (0.5)	**37.6^{a} (1.9)**	15.9^{ab} (1.0)	16.2^{c} (2.0)	11.8^{ab} (1.2)	3.4^{c} (0.4)	**47.3^{c} (1.4)**
SP	40	11.5^{a} (1.7)	13.9^{a} (0.9)	10.3^{abc} (2.5)	4.7^{c} (1.0)	**40.5^{a} (2.9)**	15.8^{ab} (3.6)	15.7^{cd} (0.7)	13.5^{ab} (3.2)	4.0^{c} (1.0)	**48.9^{bc} (1.8)**
SP	80	11.6^{a} (1.7)	13.9^{a} (1.3)	9.3^{bc} (1.0)	4.2^{c} (0.1)	**38.9^{a} (2.8)**	16.0^{ab} (2.6)	18.8^{ab} (1.9)	14.1^{ab} (1.6)	3.7^{c} (0.6)	**52.6^{ab} (2.6)**
SP	100	12.4^{a} (0.8)	13.4^{a} (0.8)	9.0^{bc} (1.4)	4.4^{c} (1.0)	**39.3^{a} (2.6)**	18.4^{a} (0.8)	20.5^{a} (0.3)	13.9^{ab} (1.6)	4.0^{c} (1.1)	**56.8^{a} (2.7)**
Al-DPS	40	11.3^{ab} (1.5)	14.0^{a} (0.8)	10.1^{abc} (0.1)	4.8^{c} (0.6)	**40.2^{a} (2.1)**	13.5^{bc} (1.3)	16.5^{bc} (2.0)	12.8^{ab} (1.1)	4.1^{c} (0.3)	**46.9^{c} (4.0)**
Al-DPS	80	11.9^{a} (0.5)	12.9^{ab}(0.8)	10.8^{abc} (1.4)	5.3^{bc} (1.4)	**40.9^{a} (2.5)**	14.5^{b} (1.4)	16.7^{bc} (0.8)	12.1^{ab} (2.4)	5.1^{bc} (0.8)	**48.4^{bc} (4.9)**
Ca-DPS	40	5.7^{c} (0.5)	11.2^{b} (0.4)	11.9^{a} (2.3)	6.3^{ab} (0.5)	**35.1^{a} (2.3)**	7.8^{e} (0.4)	11.9^{f} (1.2)	14.8^{a} (3.9)	6.4^{ab} (1.2)	**41.0^{de} (4.8)**
Ca-DPS	80	0.39^{d} (0.3)	4.4^{c} (1.1)	10.1^{abc} (1.3)	6.8^{a} (1.7)	**21.7^{b} (0.4)**	None detectible[***]	6.2^{g} (0.3)	14.0^{ab} (2.0)	7.6^{a} (3.5)	**25.7^{f} (2.2)**
Biochar	40	10.7^{ab} (0.6)	13.9^{a} (0.7)	9.6^{abc} (1.9)	4.7^{c} (0.7)	**39.0^{a} (3.6)**	11.1^{cd} (0.5)	13.6^{def} (2.0)	12.8^{ab} (1.3)	3.5^{c} (0.5)	**41.1^{de} (0.6)**
Biochar	80	9.6^{b} (1.2)	14.2^{a} (1.3)	11.3^{ab} (1.3)	4.8^{bc} (0.3)	**39.9^{a} (3.0)**	11.8^{cd} (1.3)	14.6^{cde} (2.0)	14.1^{ab} (0.7)	4.0^{c} (0.6)	**44.4^{cd} (2.3)**

[*] SP: super phosphate; Al-DPS: aluminium rich activated sludge; Ca-DPS: calcium rich lime treated activated sludge.

[**] 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 ($n = 3$).

[***] Laboratory analysis was impossible because the grass yield was too low.

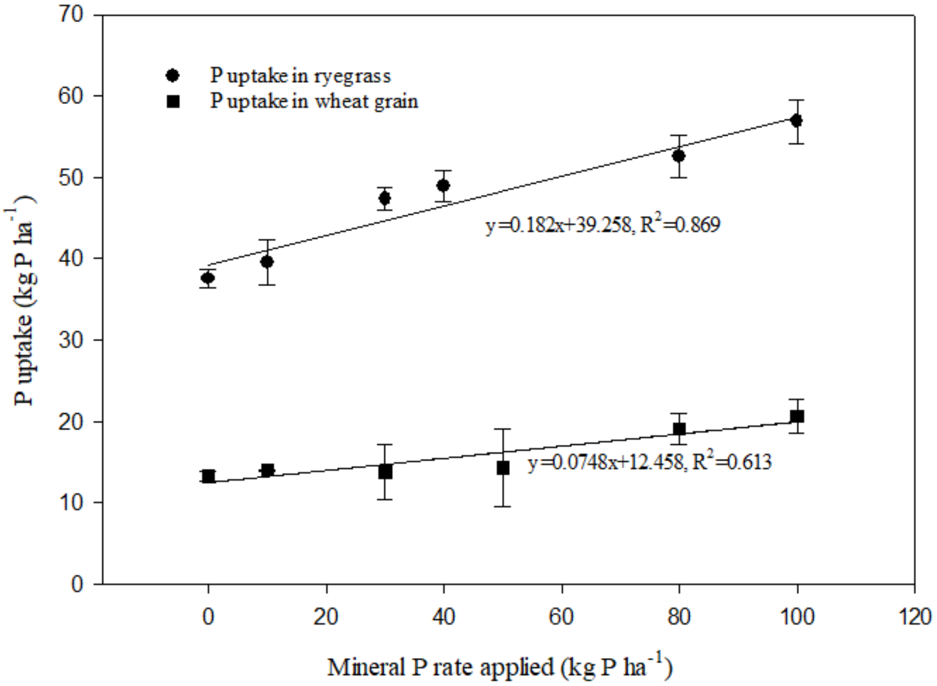

Figure 4.5 Response curve between P uptake in ryegrass, spring wheat grain and P application rate.

Table 4.9 Effect of treatment and P rate on spring wheat dry matter yield over the course of the P-MFE experiment.

Treatment[*]	P rate	Harvest[**]			
		Chaff	Grain	Chaff	Grain
	kg ha^{-1}	Yield (g)		P uptake (kg P ha^{-1})	
SP	0	19.2^{a} (2.0)	13.6^{a} (2.4)	2.3^{ab} (0.8)	13.2^{bc} (0.6)
SP	10	16.5^{a} (3.4)	12.0^{a} (2.1)	2.8^{ab} (0.2)	14.0^{bc} (0.1)
SP	30	16.2^{a} (3.2)	11.7^{a} (0.7)	2.4^{ab} (0.9)	13.8^{bc} (3.4)
SP	50	17.6^{a} (4.8)	10.9^{a} (1.6)	3.6^{ab} (2.7)	14.3^{bc} (4.8)
SP	80	18.7^{a} (5.4)	13.7^{a} (1.0)	4.9^{ab} (0.8)	19.0^{ab} (1.9)
SP	100	18.1^{a} (5.9)	13.9^{a} (2.8)	4.9^{ab} (1.0)	20.6^{a} (2.0)
Al-DPS	50	20.1^{a} (2.9)	13.3^{a} (3.0)	4.9^{a} (2.4)	16.6^{abc} (1.1)
Al-DPS	80	20.9^{a} (2.5)	12.6^{a} (4.6)	3.4^{ab} (2.1)	15.5^{abc} (3.1)
Ca-DPS	50	19.7^{a} (2.5)	15.0^{a} (1.1)	1.9^{b} (0.6)	14.9^{bc} (4.1)
Ca-DPS	80	18.0^{a} (3.6)	11.4^{a} (0.4)	2.3^{ab} (1.8)	15.1^{bc} (1.8)
Biochar	50	17.8^{a} (2.1)	12.2^{a} (1.3)	3.9^{ab} (3.0)	13.1^{c} (3.2)
Biochar	80	16.1^{a} (1.1)	11.7^{a} (1.0)	4.1^{ab} (1.6)	12.4^{c} (2.0)

[*] SP: super phosphate; Al-DPS: aluminium rich activated sludge; Ca-DPS: calcium rich lime treated activated sludge.

[**] 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 ($n = 3$).

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 chaff or grain and the control.

The P-MFE results using the two methods are presented in Table 4.7. 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% to 110.0% for spring wheat grain (Table 4.7). 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 4.4), 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.

4.3.4 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., 2022). A MFE determination of DPS can quantify their fertiliser value and provide sound advice to farmers pertaining to their sustainable use, as well as promoting their 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).

4.4 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.

Summary

This chapter quantified the MFE of two types of DPS and a DPS-derived biochar in a six-month pot trial and indicated gave an assessment that if these products had potential to be good alternative fertilisers. The effect of application rates and calculation methods on the MFE results was also estimated. The next chapter will examine the P-MFE of a range of DPS-derived STRUBIAS products.

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Chapter 5 Fertiliser equivalent value of dairy processing sludge-derived STRUBIAS products using ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum*)

This chapter presents a pot study that investigated P-MFE of a range of DPS-derived STRUBIAS products to grow ryegrass and spring wheat. It has been submitted to the Nutrient Cycling in Agrocecosystems (Special Issue on Bioeconomy) (Shi et al., 2022. Fertiliser equivalent value of dairy processing sludge-derived STRUBIAS products using ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum*)). Wenxuan Shi developed experiment design, set up the pot trial, and analysed samples from it. She is the primary author of this article.

Fertiliser equivalent value of dairy processing sludge-derived STRUBIAS products using ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum*)

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Abstract

Struvite, biochar and ash products (collectively known as STRUBIAS) products derived from different waste streams are used as fertilisers in agriculture. Raw dairy processing sludges (DPS) show promise as bio-based fertilisers, but their STRUBIAS-derived equivalents have not yet been tested as fertilisers. The objective of this study was to calculate the equivalence of phosphorus mineral fertiliser equivalency (P-MFE) using the apparent P recovery (APR) method for Fe-DPS and DPS-derived struvites (Struvite1-4), hydrochars (HC1-3) and ash and, for the first time, to quantify their suitability as fertilisers for ryegrass (*Lolium perenne L.*) and wheat (*Triticum aestivum*). The results of the P-MFE pot trials showed that the products can be divided into two groups: (1) a range of products that can (i.e., Struvite1-3) 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. Processing solutions are available to overcome agronomic performance deficits for some products. These include, for example, the avoidance of Fe dosing salts (in the case of struvite) by using biological methods of P removal or utilisation of oxalic acid during struvite precipitation, which removes Fe from the process chain and produce higher yields. Future policy and research must be aware that not all STRUBIAS products are suitable as fertilisers and therefore need to be tested individually.

Keywords: agriculture; bioeconomy; circular economy; bio-based fertilisers.

5.1 Introduction

In the European Union (EU) the dairy industry is the largest industrial food wastewater contributor. 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 chemistry based on the chemical used to treat waste (i.e., Al, Fe, or Ca), all of which have different nutrient and metal profiles and mineral fertiliser equivalence values (MFEs) (Ashekuzzaman et al., 2019; Shi et al., 2022). Similar to other organic fertilisers, land application occurs only at certain times of the year (Sommer and Knudsen, 2021), which requires costly storage and potential nitrogen (N) losses through gaseous emissions. Therefore, technologies that process raw DPS on site, whilst recovering energy and nutrients, are cost efficient. Conversion of DPS (with the addition of other feedstocks) into struvite, biochar or ash (collectively called STRUBIAS) before land application is one such technology (Shi et al., 2021; Hu et al., 2022). STRUBIAS materials are recognised as fertilisers in the EU (EC, 2019; Huygens et al., 2018) and are expected to be available 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 profiles (Shi et al., 2021). Significantly, 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). Since struvite normally has similar fertiliser efficiency with common mineral P fertilisers such as super phosphate (SP) and triple superphosphate, it is considered as a good slow-release fertiliser (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 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 (13.7%-25.7% P_2O_5; Xu et al., 2012).

DPS could be a potential feedstock for STRUBIAS material, but there is a knowledge gap on its phosphorus fertiliser equivalent value (P-MFE). This is because STRUBIAS materials are mainly P recovery products. Therefore, the objective of this study is to examine the P-MFE of a range of DPS-derived STRUBIAS products and, where there is a shortfall in agronomic performance, to suggest processing solutions to overcome such shortcomings. The results can give guidance to the fertiliser and agricultural industries with respect to these new emerging bio-based fertilisers and their efficacy.

5.2 Materials and methods

5.2.1 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. Struvite 1, 2 and 3 were precipitated from cheese production wastewater (whey) 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 this was reached, the stirrer was operated at 25 rpm (HC2) and 36 (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, a Jenway 3510 pH meter was used. Nutrients and metals were examined by an Agilent 5100 synchronous vertical dual view inductively coupled plasma optical emission spectrometer, and a high temperature combustion method was used to determine total carbon (TC) and total nitrogen (TN). Mineral N was analysed colorimetrically following with 0.1M HCl extraction.

5.2.2 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 as outlined in Shi et al. (2022). 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. Distilled water was added to reach a 70% WHC target. Finally, each layer of soil was compacted using a circular disk to a target dry bulk density of 1.2 g cm^{-3}.

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. 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) was also included in the experiments for each crop.

Chemical fertilisers (i.e., CAN, MOP and SOP) were applied to all pots to ensure that P was the only limiting nutrient (Table 5.1 and 5.2). Every treatment had three replications.

Table 5.1 Spring wheat pot design for P-FEV experiment.

Treatment	Product amount				
	CAN[1] (kg N ha^{-1})	SP[1] (kg P ha^{-1})	MOP[1] (kg K ha^{-1})	SOP[1] (kg S ha^{-1})	STRUBIAS materials (kg P ha^{-1})
Control	200	-	130	20	-
SP	200	50	130	20	-
Struvite1	200	-	130	20	50
Struvite2	200	-	130	20	50
Struvite3	200	-	130	20	50
Ash	200	-	130	20	50
HC1	200	-	130	20	50
HC2	200	-	130	20	50
HC3	200	-	130	20	50
Fe-DPS	200	-	130	20	50

Abbreviations used in table: 1 CAN=calcium ammonium nitrate, SP=super phosphate, MOP=potassium chloride, SOP=sulphate of potash, HC=hydrochar

The fertiliser application rates was based on the advised rates in Ireland (Teagasc, 2020).

Table 5.2 Ryegrass pot design for the P-MFE experiment.

Treatment	Product amount				
	CAN[1] (kg N ha^{-1})	SP[1] (kg P ha^{-1})	MOP[1] (kg K ha^{-1})	SOP[1] (kg S ha^{-1})	STRUBIAS materials (kg P ha^{-1})
Control	150	-	160	20	-
SP	150	40	160	20	-
Struvite1	150	-	160	20	40
Struvite2	150	-	160	20	40
Struvite3	150	-	160	20	40
Struvite4	150	-	160	20	40
Ash	150	-	160	20	40
HC1	150	-	160	20	40
HC2	150	-	160	20	40
HC3	150	-	160	20	40
Fe-DPS	150	-	160	20	40

Abbreviations used in table: [1] CAN=calcium ammonium nitrate, SP=super phosphate, MOP=potassium chloride, SOP=sulphate of potash, HC=hydrochar
The fertiliser application rates was based on the advised rates in Ireland (Teagasc, 2020).

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 walk in 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 $\mu mol\ m^{-2}\ s^{-1}$. All pots were held between 70 and 80% WHC by regularly weighing them. The grass was manually cut 4 cm above soil level after reaching a length of 22-26 cm and wheat plants were grown to maturity (Darch et al., 2019; González Jiménez et al., 2018). The pot trial lasted 6 months. The wheat plants were grown to maturity (20 weeks) and then separated into grain and chaff + straw after harvesting (Darch et al., 2019).

5.2.3 Crop and soil sampling and analysis

Fresh harvested crop samples were oven-dried at 70 ℃ for 72 hours in perforated plastic bags. Wheat samples were separated into grain and chaff and straw (Darch et al., 2019). 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 ℃ for 72 hours and then sieved to <2 mm and analysed for nutrients and metals as for the field soil.

5.2.4 P-FEV 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 5.1) calculated from apparent P recovery (APR) (equation 5.2) was deemed most suitable to determine the P agronomic performance and is used in the current study.

$$APR(\%) = \frac{P\ uptake_{Treatment} - P\ uptake_{Control}}{Total\ P\ applied_{Treatment}} \tag{5.1}$$

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

$$\text{P-MFE } (\%) = \frac{APR_{Treatment}}{APR_{Reference}} \times 100 \tag{5.2}$$

where P-MFE is the ratio between the apparent nutrient recovery of organic residues ($\mathrm{APR_{Treatment}}$) and the mineral fertiliser applied at the same rate (‘reference’) (Cavalli et al., 2016; 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.

5.3 Results

5.3.1 Characterisation of nutrients and metals

The DPS-derived STRUBIAS products differed in their nutrient and heavy metal contents (Table 5.3). All products had high P contents, while only Struvite 1 and 2 had a high NH_4-N content, suggesting 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).

Table 5.3 Characterisation of dairy processing sludge derived STRUBIAS products

Parameters	Struvite1	Struvite2	Struvite3	Struvite4	Ash	HC*1	HC2	HC3	Fe-DPS
	7.9	8.3	8.8	9.0	9.3	6.9	7.9	7.7	7.6
TN (g kg^{-1})	43.7	29.4	11.2	4.99	1.1	37.5	29.4	36.5	68.3
NH_4-H (g kg^{-1})	40.4	15.4	0.33	1.1	0.092	0.0026	0.0031	0.0025	0.35
TP (g kg^{-1})	104.2	80.2	47.0	59.0	99.3	78.9	85.4	79.9	57.2
TC (%)	25.9	38.8	31.6	0.20	0.90	22.6	18.4	21.2	32.7
K (g kg^{-1})	7.1	7.5	6.5	7.0	26.7	13.5	8.5	12.6	15.3
Mg (g kg^{-1})	101.3	62.2	18.8	72.8	17.0	3.7	3.7	3.5	2.9
S (g kg^{-1})	0.16	0.46	0.62	0.07	11.9	3.2	12.8	8.2	4.3
Na (g kg^{-1})	2.6	8.8	31.7	65.2	20.5	2.8	1.8	2.6	3.0
Ca (g kg^{-1})	14.7	34.5	66.9	21.2	227.5	68.0	72.0	65.7	49.2
Cr (mg kg^{-1})	2.2	2.8	3.3	2.6	41.2	6.5	6.8	6.8	5.3
Cu (mg kg^{-1})	1.8	0.21	0.38	0.82	92.7	47.8	6.1	5.4	4.2
Ni (mg kg^{-1})	<0.6	<0.6	<0.6	<0.6	27.4	7.6	9.4	9.1	7.0
Pb (mg kg^{-1})	<2	<2	<2	<2	32.6	5.9	5.9	5.3	4.3
Zn (mg kg^{-1})	30.1	34.4	36.2	6.9	482.4	186.1	185.9	171.7	136.0
Al (g kg^{-1})	0.02	0	0	0.05	82.1	8.0	8.5	7.8	6.1
Fe (g kg^{-1})	0.07	0.17	0.39	31.4	7.5	177.3	199.7	183.4	128.7
Co (mg kg^{-1})	<0.3	<0.3	<0.3	<0.3	4.9	11.0	11.3	11.0	9.6
Mo (mg kg^{-1})	<0.5	<0.5	<0.5	<0.5	11.1	<0.5	<0.5	<0.5	<0.5
Mn (mg kg^{-1})	0.53	0.57	2.24	10.2	609.6	234.7	247.9	230.3	181.7
Cd (mg kg^{-1})	<0.15	<0.15	<0.15	<0.15	0.68	<0.15	0.25	<0.15	<0.15
As (mg kg^{-1})	<1.5	<1.5	<1.5	<1.5	4.1	<1.5	<1.5	<1.5	<1.5
B (mg l)	2.0	2.7	3.0	7.4	74.0	3.1	2.0	2.4	1.7
Se (mg kg^{-1})	<1	<1	<1	<1	<1	<1	<1	<1	<1

Abbreviations used in table: *HC=hydrochar

5.3.2 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 5.4). 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. In the spring wheat study, there was no significant difference between chaff and grain yields of the control and all treatments, except ash for chaff (Table 5.5). 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.

Table 5.4 Effect of treatment and P rate on the grass dry matter yield and P uptake over the course of the P-MFE experiment across 3 harvests in 6 months.

Treatment	P rate	Harvest[1]							
		1	2	3	**cumulative**	1	2	3	**cumulative**
	kg ha^{-1}		Yield (g)				P uptake (kg P ha^{-1})		
Control	0	2.6^{d} (0.8)	2.0^{f} (0.5)	1.9^{f} (0.3)	**6.5^{f} (1.0)**	3.2^{d} (1.1)	2.7^{c} (0.6)	1.7^{f} (0.2)	**7.6^{d} (0.8)**
SP	40	5.1^{bc} (1.8)	5.3^{a} (1.5)	8.8^{a} (1.5)	**19.2^{a} (2.9)**	8.7^{a} (3.0)	5.9^{a} (1.8)	5.2^{a} (0.7)	**19.8^{a} (3.8)**
Struvite1	40	5.7^{bc} (0.8)	4.4^{abc} (1.1)	7.6^{bcd} (0.1)	**17.7^{ab} (2.2)**	5.6^{bc} (1.3)	5.4^{ab} (1.9)	4.6^{ab} (0.1)	**15.7^{bc} (1.0)**
Struvite2	40	8.3^{a} (1.9)	3.7^{bcde} (0.2)	3.3^{ef} (0.9)	**15.2^{bc} (2.4)**	8.5^{a} (0.9)	4.8^{abc} (0.9)	2.8^{de} (0.5)	**16.2^{ab} (1.2)**
Struvite3	40	7.4^{a} (0.8)	4.7^{ab} (0.4)	4.0^{de} (0.4)	**16.1^{ab} (1.6)**	8.3 ^{ab}(0.9)	4.9^{abc} (1.0)	3.7ef (0.7)	**16.9^{ab} (1.1)**
Struvite4	40	3.0^{cd} (0.5)	2.7^{def} (0.3)	1.4^{f} (0.8)	**7.0^{f} (0.5)**	5.1^{cd} (1.2)	3.6^{abc} (0.7)	1.8^{ef} (0.6)	**10.5^{d} (0.8)**
Ash	40	3.5^{cd} (0.5)	2.8^{def} (0.4)	3.0^{ef} (0.1)	**8.3^{ef} (2.1)**	3.9^{cd} (0.9)	3.6^{bc} (0.8)	1.0^{f} (0.1)	**8.5^{d} (0.9)**
HC1	40	4.8^{bcd} (1.0)	4.9^{ab} (0.6)	7.4^{abc} (1.4)	**17.1^{ab} (1.0)**	5.2^{cd} (0.9)	5.2^{ab} (1.0)	4.3^{abc} (0.4)	**14.7^{bc} (1.5)**
HC2	40	3.5^{cd} (0.1)	3.3^{cdef} (0.3)	6.3^{bcd} (0.7)	**12.5^{bc} (0.3)**	4.4^{cd} (1.2)	4.2^{abc} (0.8)	3.2^{cd} (0.4)	**11.8^{cd} (1.4)**
HC3	40	4.0^{bcd} (1.2)	4.3^{abc} (0.5)	7.8^{ab} (1.0)	**16.1^{ab} (1.6)**	4.4^{cd} (1.4)	4.3^{abc} (1.2)	3.9^{bc} (0.1)	**12.6^{cd} (2.0)**
Fe-DPS	40	4.0^{bcd} (1.0)	3.8^{bcde} (0.7)	4.3^{de} (0.4)	**12.1^{cd} (1.3)**	4.8^{cd} (1.0)	4.1^{abc} (1.1)	2.0^{ef} (1.0)	**10.9^{d} (1.2)**

[1] 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. Abbreviations used in table: SP=super phosphate, HC=hydrochar

Table 5.5 Effect of treatment and P rate on spring wheat dry matter yield over the course of the P-MFE experiment.

Treatment	P rate	Harvest[1]			
		Chaff	Grain	Chaff	Grain
	kg ha^{-1}	Yield (g)		P uptake (kg P ha^{-1})	
Control	0	19.2^{ab} (2.0)	13.6^{ab} (2.4)	2.3^{ab} (0.8)	13.2^{ab} (0.6)
SP	50	17.6^{ab} (4.8)	10.9^{ab} (1.6)	3.6^{a} (2.7)	17.7^{a} (4.8)
Struvite 1	50	20.8^{a} (2.3)	14.4^{a} (1.4)	3.1^{ab} (0.4)	17.1^{a} (1.1)
Struvite2	50	20.6^{a} (3.5)	14.5^{a} (5.4)	4.8^{a} (2.5)	17.4^{a} (4.1)
Struvite3	50	19.5^{a} (2.5)	11.7^{ab} (3.3)	4.2^{ab} (2.3)	16.6^{a} (2.2)
Ash	50	11.9^{c} (3.6)	6.7^{b} (1.0)	1.2^{b} (0.3)	5.4^{d} (1.0)
HC1	50	18.8^{ab} (2.8)	10.9^{ab} (3.2)	1.7^{ab} (0.5)	11.0^{bcd} (1.2)
HC2	50	17.0^{abc} (3.1)	11.1^{ab} (4.6)	2.1^{ab} (1.2)	11.1^{bc} (3.2)
HC3	50	16.4^{abc} (0.2)	11.8^{ab} (2.5)	1.8^{ab} (0.2)	10.2^{bcd} (3.4)
Fe-DPS	50	14.2^{bc} (3.3)	8.0^{b} (2.8)	3.3^{ab} (1.9)	7.6^{cd} (2.6)

[1] 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.

Abbreviations used in table: SP=super phosphate, HC=hydrochar

5.3.3 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 5.6. 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.

Table 5.6 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 to guide agronomic advice.

	P rate **kg ha^{-1}**	**APR from Eqn. 1** **%**	**P-MFE from Eqn. 2** **%**
		Ryegrass	
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	
Struvite1	50	8.5	87.0
Struvite2	50	9.2	93.5
Struvite3	50	7.6	77.9
Ash	50	-14.8	-151.3
HC*1	50	-3.5	-35.8
HC2	50	-3.4	-34.5
HC3	50	-4.9	-50.2
Fe-DPS	50	-10.4	-106.4

[1] Struvite 4 was not used in the spring wheat trial. Abbreviations used in table: *HC=hydrochar

5.4 Discussion

5.4.1 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 alone, is flawed. Struvite products had high concentrations of P and Mg, with heavy metal concentrations lower than legal limits (EU, 2019). Struvite 1-3 was generated from cheese production wastewater (whey) with different pH and salt dosages, resulting in different nutrient profiles (Numviyimana et al., 2020). Struvite 1 was produced under optimal conditions 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. 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 heavy 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 hydrochar yield (Khalaf et al., 2022) but did not affect the HC characteristics.

5.4.2 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 fertiliser efficiency similar 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 5.4). The results of the literature show that struvite derived from different feedstocks exhibits a range of agronomic performance (Table 5.7). 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. González-Ponce et al. (2021) conducted a 90-day pot experiment with struvite derived from anaerobically digested sewage sludge on grass. High 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 and inhibitory properties of struvite (Mbamba et al., 2015). 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 phytotoxity 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 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 spring wheat yield. 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). These varying results may be influenced by the type of feedstock or the post-treatment process, which affects the solubility of P (Rubæk et al., 2006, Møller et al., 2007). 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 (a common binder in the process of granulation of various synthetic or natural substances) 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 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 is 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. For example, Melo et al. (2018) reported positive results of sewage sludge HC on the yield of Phaseolus beans. 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 chemical 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 profiling 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.

Table 5.7 Comparative agronomic value of STRUBIAS materials from non-dairy processing sludge feedstocks

Types of fertiliser	Feedstock	Production process	P concentration	Application rate	Experimental scale	APR or P-MFE	Notes	Reference
Struvite	Cattle slurry	Struvite was precipitated from liquid fraction of anaerobic digestate.	39.4 g kg^{-1}	2 g P pot^{-1}	Pot	P-MFE: 138.0 and 154.5%	Grass yield after the struvite treatments exceeded that from mineral fertiliser.	Szymańska et al. (2020)
Struvite	Sewage sludge	In a continuous stirred tank and a fluidised bed reactor	11.11% 10.35%	5.64 g P m^{-2}	Pot	APR: ~10%	Struvite increased grass yield and apparent nutrients recovery	González-Ponce et al. (2021)
Ash	Pig manure	Gasification	50-60 g kg^{-1}	20 and 60 kg P ha^{-1}	Field	P-MFE: 11-117%	Did not improve barley yield compared to control treatment.	Kuligowski et al. (2010)
Acid extract from ash	Pig manure	Treating with H_2SO_4 and neutralizing with KOH	0.192 g P l^{-1}	10, 20, and 30 kg P ha^{-1}		P-MFE: 73-111%	Has similar agronomic effectiveness as disodium phosphate	
Ash	Sewage sludge	750–1000 °C	80 g kg^{-1}	0.625, 1.25, 2.5, 5.0, 10.0 and 15.0 g kg topsoil^{-1}	Pot	N/A	Shoot dry mass of *Trifolium subterraneaum* was increased	Battisti et al. (2022)
Ash	Mix of wood chips, sawdust, and bark	300 °C	33.2 mg kg^{-1} available P	0, 10, 25 and 50 g ash pot^{-1} (5kg soil pot^{-1})	Pot	N/A	Ash application did not significantly affected wheat growth. Toxic element contents in wheat grown in contaminated soils	Ochecova et al. (2014)

							with ash addition were low and decreased, whereas the concentrations of major nutrients increased.	
Hydrochar	Sugar beet pulp, beer draff	190 °C, 12 h reaction time	0.5 and 1.0 g kg^{-1} calcium-acetate-lactate-extractable P	10 mg ha^{-1} (DM)	Field	N/A	Hydrochar reduced initial sugar beet growth.	Gajić and Koch. (2012)
Hydrochar	Sewage sludge	190 °C, pH 4.5, 4 h reaction time	11.6 g kg^{-1}	4, 8, 16 and 32 mg ha^{-1}	Pot	N/A	Hydrochar improve the yield of Phaseolus beans	Melo et al. (2018)
Hydrochar	Pinewood sawdust	Amino-functionalised hydrochar (by polyethylenimine grafting) and uncodified one	N/A	1.0%, 3.0% and 5.0%	Pot	N/A	Unmodified hydrochars produced low rice yields. Amino-functionalised increased the plant length and dry mass yield by up to 50 and 25%	Xia et al. (2020)
Hydrochar	Sugar beet pulp, beer draff	190 °C, 12 h reaction time	0.5 and 1.0 g kg^{-1} calcium-acetate-lactate-extractable P	10 mg ha^{-1} (DM)	Field	N/A	Hydrochar reduced initial sugar beet growth.	Gajić and Koch. (2012)

Abbreviations used in table: APR=apparent phosphorus recovery; P-MFE=phosphorus mineral fertiliser equivalent value; N/A=not available; DM = dry matter;

5.5 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 negative crop yields and 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 profiles, along with their agronomic performance as fertilisers.

Summary

This chapter quantified the P-MFE of different DPS-derived STRUBIAS products in a six-month pot trial and assessed if these products had potential to be good alternative fertilisers.

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Chapter 6 Conclusions and Recommendations

6.1 Overview

The global industrialisation of food production, to feed a rapidly growing population, is putting pressure on finite rock phosphate resources (Jarvie et al., 2015). In particular, the European Union (EU) urgently needs safe alternative sources of phosphorus (P) to overcome this challenge, as Europe lacks natural rock phosphate deposits of its own and mainly depends on imported P. Use of more organic P alternatives will contribute to the delivery of the EU Green Deal and support the shift to a green economy.

The dairy processing industry generates a large amount of P-rich dairy processing sludge (DPS), which currently goes to land in several countries across a variety of crops. Presently, there is little research on the agronomic performance of such alternative P products. Furthermore, raw wastes can be further processed into secondary-raw-material-based products, referred to as STRUBIAS (STRUvite, BIochar, or incineration AShes) (Huygens et al., 2018), which are a recognised group of bio-based fertilisers and are expected to be on the EU fertiliser market by 2030 (EC, 2019). However, a dearth of information pertaining to both DPS raw and DPS-derived STRUBIAS products (i.e., variability in their nutrient and metal content, their fertilisation potential, risks associated with their use) prevents their proper incorporation into nutrient management planning, which aims to simultaneously achieve both environmental and agronomic goals. Currently, agronomic performance is based not on trials with crops but on the ad-hoc nutrient profile of these products. This is flawed as all of these products are heterogeneous and have a temporal profile. This over-simplification of bio-based products is also not good practice and neglects the role of both soil and plant in ascertaining bio-based products' mineral fertiliser equivalency.

Therefore, this research aimed to provide a thorough investigation of different DPS and DPS-derived STRUBIAS products, including (1) their nutrient and metal characterisation (2) their nitrogen (N) and P mineral fertiliser equivalent value (N- and P-MFE) when used to grow ryegrass and spring wheat, and (3) the effect of different application rate (optimal versus high) and calculation methods (with and without chemical fertiliser response curves) on the MFE. Addressing these knowledge gaps may help to inform farmers, advisors and growers about their agronomic value, identify any potential environmental risks arising from their use in agricultural land production, and offer advice about the potential for their incorporation into farm nutrient management plans. In addition, a MS Excel^{TM} programme was created based on the above studies to provide farmers with a quick and safe way to reuse these products.

6.2 Conclusions

The main conclusions of this study are:

- DPS and DPS-derived products have potential to be valuable alternative fertilisers. However, due to their physico-chemical characteristics, there were significant differences within each group: Al-DPS had high MFE, while Ca-DPS had low MFE, although its slow P release indicated that it may have long-term potential to be a good fertiliser. Only three of the four struvites had good agronomic performance (the struvites precipitated from dairy wastewater), whereas the MFE of the fourth struvite (precipitated from hydrochar liquid) and all the hydrochars had poor agronomic performance. These products were limited by their high Fe contents introduced during wastewater treatment to remove P. Ash and biochar had no MFE and cannot be used in agriculture directly.
- The results of application rate and how it affects MFE were variable: High-rate applications of DPS only improved N-MFE of ryegrass, but not N-MFE of spring wheat

grain and P-MFE. This indicated that over-fertilisation is unnecessary and should be avoided. There is no difference between two different calculation methods for MFE (with and without response curves), which means that only one rate of mineral fertiliser P (the 'reference') should be used instead creating a response curve using different application rates. There was no grass and spring wheat response to increasing mineral P fertilisation. This may be because the applied P was precipitated and fixed by Al_3^+ and Fe_3^+ in the soil. The poorly soluble P complexes were easily formed with aluminium and iron in acidic soil and cannot be absorbed by crops. However, more soil studies are needed to explain this question. For example, the 33P isotope dilution technique used in recent work by Komenko et al. (2023a,b) may help to answer it. This technique can assist in understanding of P build-up mechanism.

- Since the MFE of different products varied greatly, generic fertiliser guidelines, based on a particular group of bio-based fertilisers, are flawed. In addition, many parameters, such as the scale and duration of the vegetation trial, tested plant and soil used, can affect the MFE results. A standardised methodology, therefore, should be used to test every bio-based fertiliser for their agronomic performance before their reuse in agriculture.
- The chemical characteristics of DPS and DPS-derived STRUBIAS varied greatly in accordance with the types of dairy products, wastewater treatment system, and processing methods. All these products had high P concentrations. Nitrogen was high in DPS but low in the thermo-chemical STRUBIAS products.

6.3 Future work and recommendations

The recommendations arising from this study are:

- A centralised database on the nutrient and metal content of different types of DPS and DPS-derived STRUBIAS products available in Ireland should be developed and should be expanded as new products emerge. Such a database should also record the location of the lands on which they are spread. Long-term monitoring of these sites may be used to gain valuable information regarding nutrient build-up and drop-off in soils and crops over time. Companies that want to spread these products must become much more engaged and accept that these products are heterogeneous. They need to invest in high frequency testing or real-time characterisation of these products and give up-to-date advice on nutrient contents to inform application rates.
- Vegetation trials are essential to estimate the agronomic performance when a new fertiliser emerges, but many parameters, such as the scale of the trial, its duration, test plant used, the soil used, etc. will influence the outcome. Therefore, a standardised procedure to examine the agronomic performance must be applied to allow comparisons to other products to be made.
- Chemical solubility of DPS and DPS-derived STRUBIAS products may be used to quickly determine plant available P. However, since the results from chemical extractions do not satisfactorily replace vegetation trials (Kratz et al., 2019), alternative techniques are being investigated. These include sequential fractionation on incubated soil/fertiliser mixtures, in combination with an isotopic labelling approach and diffusive gradients in thin-film (DGT) extraction of incubated soil/fertiliser mixtures. These techniques have limitations: isotopic labelling requires a highly controlled laboratory which may limit routine usage, and the results from DGT extraction are soil-dependent. However, both methods need further investigation and, if combined with vegetation growth trials, may enable a standard approach to be implemented. Some of these approaches have been investigated within the REFLOW project. For example,

Khomenko et al. (2023b) investigated different DPS and P turnover and availability in soil using the 33P isotope dilution method.

- The MS EXCEL^{TM} application rate calculator developed in this study can only provide a generic guidance of maximum legal application rates. This tool could be developed further to incorporate N and P availability, and be made available as an online or phone application (digital app) to guide growers, contractors, farmers and processing plant operators, as part of on-going nutrient management planning. The advantage of the tool is that it can be adapted for country-specific conditions. In addition, guidance on emerging contaminants (provided they have legal limits in soil) could be added into the tool. Risk assessment of potential losses from the land application of these products to the environment and into the human chain could be assessed. Currently, there is a lack of information (or register) as to where these products go to land and indeed how much volume goes to such land parcels.
- This study had a relatively short duration. Although some products like Ca-DPS did not show good agronomic performance during the experiments, they may prove to be more valuable in long-term fertilisation studies. Long-term pot or field trials can provide more information of their fertiliser value and would be needed in the future. The potential environmental risks of these products, including the bioaccumulation of contaminants in soil and crops and nutrient losses to water, soil and air, need to be estimated through field study before they are applied in large-scale studies.

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Appendix A

Shi, W., Healy, M. G., Ashekuzzaman, S. M., Daly, K., Leahy, J. J., Fenton, O., 2021. Dairy processing sludge and co-products: A review of present and future re-use pathways in agriculture. Journal of Cleaner Production, 314, 128035. https://doi.org/10.1016/j.jclepro.2021.128035

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Dairy processing sludge and co-products: A review of present and future re-use pathways in agriculture

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ABSTRACT

The dairy industry is one of the largest global producers of wastewater and generates huge volumes of dairy processing sludge (DPS). There are two main types of DPS, lime-treated dissolved air floatation sludge and biochemically-treated activated sludge. These sludge types may also be converted to STRUBIAS (STRUvite, BIochar, AShes) products which have potential as fertilizers, secondary feedstocks for phosphate fertiliser granules, and soil amendments. A small number of studies indicate that these products have variable nutrient and metal contents, which differ across sludge and STRUBIAS product types. This is due to many factors such as the type of dairy plants, wastewater treatment process and production technologies. Although such products are land applied, the phosphorus (P) and nitrogen (N) fertilizer equivalency value (FEV) are often unknown and not factored into application rates, and therefore need study under field conditions (across soil and crop types). This review identifies a need to quantify antimicrobial drugs, hormones, pesticides, disinfectants, persistent organic pollutants (POPs), microplastics and nano-particles in all DPS and STRUBIAS types. Where detected, testing should follow the transfer of these contaminants to the soil, crop and water continuum. Further knowledge in the areas identified would enable both agronomic and environmental goals to be met and promote higher uptake of DPS and STRUBIAS re-use in agriculture.

1. Introduction

In the aftermath of the COVID-19 pandemic and the associated economic downturn, the world's food system will be under threat and must become more sustainable and resilient (EC, 2020). The recently published Farm to Fork Strategy of the European Union (EU) aims to accelerate the transition to a sustainable food and agriculture system (EC, 2020). One of the recommended practices is to reduce excess fertilisation and to foster the recycling of nutrients from different kinds of organic waste as fertilisers. This will contribute to the delivery of the "zero pollution ambition" of the EU Green Deal (EC, 2020). The European Commission (EC) has recently revised the EU Fertiliser Regulation (EC, 2019), expanding its scope to include secondary-raw-material-based fertilising products to support the shift to sustainable agriculture and a "circular economy" (Huygens et al., 2018). In particular, the EU needs safe recycling sources of phosphorus (P), as Europe lacks natural phosphate rock deposits and mainly depends on imported P. Exploring alternatives to mineral P fertilisers and increased recycling of P may substantially contribute to the reduction of demand for fossil P resources and the dependency on the importation of P from other countries (Arenas-Montaño et al., 2021).

The reuse of raw materials that are now disposed of as waste is one of the key principles of sustainable agriculture and the circular economy. As one of the largest agricultural sectors in the EU (Augère-Granier, 2018), the dairy industry is now considered to be the largest global industrial food wastewater source and one of the main sources of P-rich industrial effluents (Kolev Slavov, 2017; Erkan et al., 2018). To meet discharge limits, dairy wastewater must be treated before discharge. It can be either discharged along with other wastewaters into municipal wastewater treatment plants (WWTPs) or treated on site if dairy plants have their own WWTP. As conventional wastewater treatment systems are used, a large volume of solid organic wastes is generated. These are referred to as dairy processing sludge (DPS) when the dairy wastewater is treated on site (Ashekuzzaman et al., 2019a).

According to current practices in the EU, DPS is categorised as a biosolid (Pankakoski et al., 2000), and therefore can be spread on

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agricultural lands (arable and grassland) as it is rich in both the macro- and micro-nutrients required for healthy plant and animal growth (Ryan and Walsh, 2016). It also has potential to be used as an additive in compost, animal feed, biofuel, or it may be dried and incinerated (Korsström and Lampi, 2001; Ryan and Walsh, 2016). However, very few studies focus on DPS specifically. The fertiliser value and the possible environmental risk of DPS have not been studied in any great detail, and such knowledge gaps prevent such products from being recognised as sustainable marketable products. For example, the fertiliser value of DPS, which is an important parameter for farmers and agricultural advisors to know before land application, is rarely reported. It is significantly affected by the type of dairy plants, e.g. cheese factories generally have 50% more P than fresh milk dairies (Kwapinska et al., 2019). Therefore, more studies and tests should be conducted across the DPS from different factory to avoid improper landspreading. Moreover, although the heavy metal concentration of DPS has been reported to be low (Kwapinska et al., 2018; Pankakoski et al., 2000), some emerging organic pollutants may be present in DPS due to their lipophilic properties. The contamination of the soil with these emerging compounds, as a result of the DPS application, could be transferred to the plants via the roots into different plant tissues (Navarro et al., 2017). This would discourage many food companies from using crops or products (e.g. grazing of animals) originating from land amended with DPS (Perkins, 2019). There are also other concerns related to the use of DPS for land spreading. DPS decomposes quickly and releases strong odours due to high fat, oil and grease (FOG) and total suspended solids (TSS) content (Atallah et al., 2020; Bharati and Shinkar, 2013). Therefore, it cannot be stored for long periods and as the transport costs are high, it is commonly spread on lands in the vicinity of the dairy factories. Since the land bank of the nearby lands that can receive DPS is limited, it is easy to cause local oversupply of DPS, potentially leading to the accumulation of nutrients in soil, which may ultimately damage the aquatic ecosystem (Healy et al., 2016; Peyton et al., 2016). Weather conditions also constrain land spreading. For example, the land application of DPS is prohibited during the closed period over winter (i.e. hydrologically active period) in Ireland (S.I. No 378/2006). For these reasons, DPS cannot be fully utilized for land spreading. In the long term, there is a need to find alternative treatment and disposal methods of DPS. Secondary-raw-material-based fertilising products, which are referred to as STRUBIAS (STRUvite, BIochar, or incineration AShes), have already been recognised as fertilisers by EU to address this issue (EC, 2019; Huygens et al., 2018). STRUBIAS materials derived from wastewater and sludge are expected to be on the EU fertiliser market by 2030 and to be safe and effective alternatives for mined rock phosphate and processed P fertilisers (Huygens et al., 2018).

Knowledge gaps pertaining to present and future re-use of DPS and STRUBIAS products in agriculture still remain. Before these products can be deemed sustainable and safely used in agriculture, these aspects need to be reviewed and recommendations presented. Therefore, this paper aims to review present and future re-use pathways and potential challenges for these products in agriculture. Identification of such knowledge gaps will give the dairy processing and agricultural industries guidance on future research that is needed and may add value to the supply chain of the dairy production process.

2. Methodology

The review was carried out using scientific literature from databases and search engines including Google Scholar, American Chemical Society (ACS), Science Direct, Scopus, Springer Nature, Wiley and Web of Science. A detailed search of DPS and co-products reuse in agriculture in relevant literature was completed using the following keywords: dairy waste, dairy processing sludge, dairy wastewater treatment, STRUBIAS, struvite, sludge ash, biochar, fertiliser, fertiliser replacement/equivalent value, phosphorus, recovery, recycling, reuse, and emerging contaminants. Various combinations and derivations of the keywords were used.

As a result of these search criteria, 136 scientific papers were selected, from which about 45% were published in the last 5 years and 70% in the last 10 years. A deeper analysis was conducted on these papers and relevant information was extracted such as: dairy wastewater treatment methods, properties of DPS and current practices, fertiliser efficiency of DPS, potential environmental risk of DPS application, potential co-products derived from DPS and potential use in agriculture.

3. Dairy processing sludge characterisation

3.1. Current knowledge of dairy effluent nutrient and metal content

The dairy industry produces various products such as sterilised and pasteurised milk, yogurt, ice cream, butter, cheese, and milk powder, with different processes taking place such as pasteurization, coagulation, filtration, centrifugation and chilling (Carvalho et al., 2013). Dairy effluents vary significantly both in quantity and quality based on dairy factory characteristics (Janczukowicz et al., 2008) (Tables 1 and 2). The flow rates of dairy effluents vary due to scale, products, techniques, processes and equipment (Gutiérrez et al., 1991), and may also vary diurnally (Danalewich et al., 1998). Milk processing rates are typically higher in summer and lower in winter, and result in high seasonal variations in wastewater volume and properties (Janczukowicz et al., 2008). Moreover, the composition of these effluents varies greatly depending on the different types of products, system and operation methods (Carvalho et al., 2013). The effluent generally comprises dilutions of milk (or milk constituents including lactose, minerals, fat, whey and protein) lost in the technological cycles, starter cultures used in manufacturing, by-products (whey, milk and whey permeates), residues and contaminants from washing milk containers, equipment and floors, disinfectant applied in clean-in-place (CIP) processes, and other additives that may be used (Ahmad et al., 2019; Kolev Slavov, 2017). Dairy processing effluent is distinguished by high concentrations of organics and nutrients, and a pH varying from 4 to 12. Such a large variation of the pH is attributed to the use of acid and alkaline detergents and sanitizers for washing (Britz et al., 2006). The residues of milk and milk by-products in the waste stream result in higher nutrient and organic contents than those normally present in domestic wastewater (Booker et al., 1999). Suspended solids are derived from coagulated milk, cheese curd, or flavouring ingredients (Demirel et al., 2005). High concentrations of sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) have been measured in the wastewater, while heavy metals may be also present in low concentrations (Table 3).

3.2. Current knowledge of DPS nutrient and metal content

Dairy wastewater must be treated to meet licensed discharge limits before discharge to surface water bodies. Normally, there are three main stages of wastewater treatment (Fig. 1). Primary treatment consists of sedimentation/physical screening to remove large particles or debris, flow and composition balancing to stabilize effluent, chemical addition to control pH, and dissolved air floatation (DAF) to remove FOG (Ryan and Walsh, 2016). Two types of biological degradation systems, aerobic and anaerobic systems, can be used in secondary treatment to remove organic materials. Large quantities of DPS are produced during this stage and pollutants can be absorbed into it. Aerobic biological techniques, including activated sludge process, sequencing batch reactors, bio-towers or membrane bioreactors, are carried out using dissolved oxygen (Ryan and Walsh, 2016). This is a reliable and cost-effective treatment in producing a high-quality effluent, but results in high DPS generation (0.6 kg dry DPS per kg of biochemical oxygen demand (BOD_5) removed) and costly disposal problems (Britz et al., 2006). Frequently used anaerobic biological technologies involve anaerobic lagoons, up-flow anaerobic sludge blankets, membrane anaerobic reactor systems, and completely stirred tank reactors (Britz et al., 2006). Less DPS is generated during anaerobic digestion than during aerobic

Table 1
DPS generation (per unit volume/mass of processed milk) and disposal pathways in different countries.

Region	Water consumption	Effluents loads	DPS volume	Method of Disposal	Reference
EU	0.2–11 L/L processed milk	0.3×10^6–3×10^6 L (in a factory with capacity:10^6L milk/day)	1-3t dry matter sludge (in a factory with capacity: 10^6L milk/day)	Wastewater: drained to rivers sludge: land spread	Daufin et al. (2001)
EU	0.8–60 m^3/t processed milk	0.9–60 $m3^3$/t processed milk	0.2–30 kg sludge/t processed milk	–	EC (2006)
Sweden	0.96–4.0 L/L processed milk	0.86–4.3 L/L processed milk	–	Landfill, compost, irrigation, biogas production. In Denmark, 2/3 sludge from dairies is irrigated on cultivated land and the rest is utilized in biogas production.	Korsström and Lampi (2001)
Denmark	0.60–1.9 L/L processed milk	0.75–1.5 L/L processed milk	–		
Finland	1.2–4.6 L/L processed milk	1.2–3.9 L/L processed milk	–		
Norway	2.5–6.3 L/L processed milk	2.0–3.3 L/L processed milk	–		
Ireland	2.3 m^3/m^3 processed milk	2.71 ± 0.9 L/L processed milk	15–19.7 kg sludge/m^3 milk processed	Sludge: land spread (63%), compost (13.6%), or removed by licensed contractors (23.4%)	Ashekuzzaman et al., (2019a); Ryan and Walsh (2016)
Australia	0.07–2.90 L/L milk	–	31 kg organic waste/t product	Compost, fertiliser, stockfeed and recovery of marketable products.	Prasad et al. (2004)
United States	–	0.10–12.4 kg/kg milk	~213	Effluent: discharge into municipal sewage treatment system or irrigate on the land	Durham and Hourigan (2007)
United States	–	170–2081 m^3/d	–		Danalewich et al. (1998)
UK	1.8 L/kg product	1–5 L/L processed milk	–	Sludge: landfilling	Klemes et al. (2008)

processes (Britz et al., 2006). Phosphorus is removed in tertiary treatment through the use of chemicals like aluminium (Al) and/or iron (Fe) salts, before final discharge (Britz et al., 2006; Ryan and Walsh, 2016). Recently, the enhanced biological phosphorus removal (EBPR) process, without the need for chemical precipitants, has received increased attention. EBPR is achieved through the activated sludge process by recirculating sludge through anaerobic and aerobic conditions (Oehmen et al., 2007).

The wastewater treatment processes within a dairy processing plant generates a specific DPS type, which can be predominantly categorised into (1) lime-treated DAF sludge and (2) bio-chemically-treated activated sludge (Ashekuzzaman et al., 2019a). The former is produced after chemical and DAF treatment of raw wastewater during primary treatment. The latter is stabilized sludge from secondary biological degradation treatment, which can be either aerobic or anaerobic, or a combination of the two.

As DPS is categorised as a biosolid, it is commonly landspread in agricultural areas (Ryan and Walsh, 2016). DPS is a relatively new waste type and it is a much cleaner and valuable fertilising product than biosolids derived from sewage sludge, but it is rarely studied specifically. So far, very few studies have investigated the properties and fertilising effect of DPS. López-Mosquera et al. (2000) used DPS as a fertiliser for grassland and found that the heavy metal content didn't lead to harmful accumulation of metals in the short- or medium-term (4 years) (Table 4). Ashekuzzaman et al. (2019a) collected and characterised 63 DPS samples covering 9 major dairy processing companies of Ireland and found that the nutrient content varied across different sludge types (Table 4). The reported values of heavy metals in DPS (Table 4) were found to be lower than the EU upper limit thresholds recommended for bio-based fertiliser (EC, 2019), which indicates their relatively low metal bioaccumulation risk if used in agriculture.

4. Fertiliser equivalent value (FEV) of DPS

The efficiency of most bio-based fertiliers is normally unstable and lower than chemical fertilisers because of their relatively low nutrient content, slow nutrient release rate and highly variable nutrient composition (Chen, 2006). Therefore, the agronomic value of DPS should be determined before they are used in agriculture, which will make farmers more confident to use them. The FEV is defined as the application rate of mineral fertiliser to which the fertilisation effect of bio-based fertilisers on crop yield or nutrient uptake is equivalent (Brod et al., 2012).

The FEV can both provide a quantitative estimate of the amount of efficient nutrients in bio-based fertiliser and a theoretical estimate of its actual price in comparison to a mineral fertiliser. This can give farmers information about how to use bio-based fertilisers and the economic impacts associated with their use (Ashekuzzaman et al., 2019a). However, the results of FEV may vary widely, as FEV is not only affected by the assessment method, but also by factors like type of bio-based fertilisers, crop type, fertiliser application time (Delin, 2011), rates (Hijbeek et al., 2018), and method (Lalor et al., 2011).

To date, studies of FEV have mainly focused on the fertiliser equivalent value of nitrogen (N) (FEV-N) of manure and slurry. Research on the FEV (both FEV-N and fertiliser replacement value of P (FEV-P)) of DPS is scarce. Ashekuzzaman et al. (2021) applied an agronomic trial in grassland with four representative DPS to determine both the FEV-N and FEV-P of DPS. The FEV-N of DPS samples was observed to be between 8 and 54%, but the FEV-P was not derived as the experimental site was non-responsive to increasing mineral P rate. Ashekuzzaman et al. (2019a) provided a theoretical estimation of the FEV for the four types of Irish DPS from the total nutrient concentration (N, P, K), which showed a wide variation due to the considerable variation of DPS properties. In addition, the crop available fraction of N and P is still not well understood, which would play a vital role on the fertiliser value of DPS. The wastewater treatment process may have a significant effect on the plant available N and P. The ammonium-N (NH_4–N) concentration, which is easily plant available N, would decrease significantly with the use of lime (Libhaber and Orozco-Jaramillo, 2012), but may increase after an anaerobic digestion process (Mtshali et al., 2014). This effect on the plant availability of P is more complicated. Krogstad et al. (2005) found that the P fertilising effect of sludge with biological purification without chemical additives and lime treatment could be comparable to mineral P fertiliser, whereas P fertiliser value of sludges precipitated by use of Fe and Al salts without liming treatment was very low. Kahiluoto et al. (2015) found P was more available in sludge with a moderate Fe/P ratio (1.6), but had an adverse effect on the plant-availability of soil P with a surplus Fe coagulant (Fe/P of 9.8). Some studies have indicated that liming increases the plant-available P in sludge produced from the wastewater treated by Al and/or Fe salts (Bøen and Haraldsen, 2013; Krogstad et al., 2005; Montgomery et al., 2005). However, Kahiluoto et al. (2015) found that P was not available to plants in the sludge

Table 2
Characteristics of dairy waste effluent.

Effluent type	pH	BOD_5 (g/L)	COD (g/L)	TS (g/L)	TSS (g/L)	VS (g/L)	VSS (g/L)	FOG (g/L)	TN (mg/L)	TP (mg/L)	DOM (mg/L)	Reference
Milk factory	5.5–6.9	0.092–0.116	0.160–0.208	0.094–0.110							76.4–86.4	Mishra et al. (2000)
Dairy plants (produce cheese)	6.2–11.3	0.565–5.72	0.785–7.62	1.84–14.21	0.326–3.56	0.562–11.03	0.225–1.94		14.0–40.0	29–181		Danalewich et al. (1998)
Mixed dairy	4–11	0.24–5.9	0.5–10.4	0.71–7	0.06–5.8			0.02–1.92	10–660	0–600		Kolev Slavov, 2017
Milk reception	7.18	0.798	2.54		0.654			1.06				Janczukowicz et al. (2008)
Butter	12.08	2.42	8.93		5.07			2.88				Janczukowicz et al. (2008)
Cheese	7.90	3.46	11.75		0.940			0.331				Janczukowicz et al. (2008)
Cottage cheese	7.83	2.60	17.65		3.38			0.950				Janczukowicz et al. (2008)
Cheese whey	4.46	40	60	59	1.5							Gannoun et al. (2008)
Cheese whey	4.0–4.6	10–12.5	8.8–25.6	7.0–8.3	1.6–4.8			1.83–3.76	310–356	6.6–7.2		Rivas et al. (2010)
Hard cheese whey	5.80	29.48	73.45		7.15			0.994				Janczukowicz et al. (2008)
Cottage cheese whey	5.35	26.77	58.55		8.13			0.492				Janczukowicz et al. (2008)
Ice cream	5.2	2.45	5.2	3.9		2.6			60	14		Karadag et al. (2015)
Creamery	8–11	1.2–4	2–6		0.35–1		0.33–0.94		50–60			Demirel et al. (2005)
Cleaning water	10.37	3.47	14.64		3.82			3.11				Janczukowicz et al. (2008)

BOD_5 = biological oxygen demand for 5 days, COD = chemical oxygen demand, TS = total solids, TSS = total suspended solids, VS = volatile solids, VSS = volatile suspended solids, FOG = fat, oil and grease, TN = total nitrogen, TP = total phosphorus, DOM = dissolved organic matter.

Table 3
Concentrations (mg/L) of trace elements in dairy waste effluent.

Effluent type	Cd	Fe	Cu	Pb	Zn	Ni	Na	K	Ca	Mg	Al	Co	Mn	Reference
Dairy plants (mainly produce yogurt)	0.090	1.181	0.350	1.095	0.234	0.166								Afolabi et al., 2016
Creamery		2–5				0.5–1.0	170–200	35–40	35–40	5–8		0.05–0.15	0.02–0.10	Demirel et al. (2005)
Cheese		0.039–4.33	0–0.03			0.012–0.071	263–1265	8.6–155.5	1.4–58.5	6.5–46.3	0.063–0.257	1–0.007	1–0.835	Danalewich et al. (1998)
Mixed dairy		0.5–6.7				0–0.13	123–2324	8–160	11–120	2–97		0	0.03–0.43	Demirel et al. (2005)

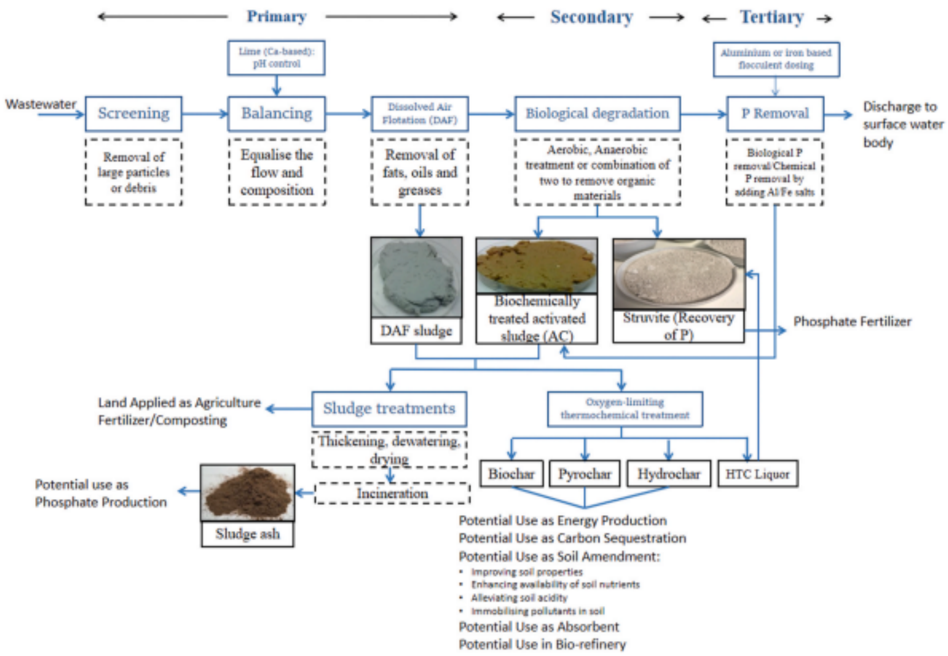

Fig. 1. Flow chart of dairy wastewater treatment process and sludge, struvite, and char generation. DAF sludge = Lime treated dissolved air flotation processing sludge; AC sludge = Bio-chemically treated activated sludge (adapted from Ashekuzzaman et al., 2019a).

Table 4
Characteristics of DPS. Adapted from Ashekuzzaman et al. (2019a) and López-Mosquera et al. (2000).

Parameters	Bio-chemically treated activated sludge "AC"[a]	Lime treated DAF sludge "DAF"[a]	Combined treated sludge "CM"[a]	Anaerobically digested sludge "AD"	Dairy-plant sludge	EU requirements of bio-based fertiliser[b]
DM (% of wt.)	13.3	25.9	16.1	3.5 ± 1.1		
OM (% of DM)	62.9	46.9	73.9	72.5 ± 1.3		
pH	7.3	7.2	6.8	7.5 ± 0.1		
TN (g/kg)	57.2	19.5	46.0	70.4 ± 1.2		>10
TP (g/kg)	36.8	65.9	20.0	14.6 ± 1.2		>10
TC (g/kg)	29.4	24.3	42.2	35.6 ± 1.2		
K (g/kg)	7.2	3.9	2.9	6.1 ± 1.1		>10
Mg (g/kg)	3.2	4.3	1.4	1.9 ± 0.1		
S (g/kg)	4.8	2.1	7.6	5.3 ± 0.7		
Na (g/kg)	5.3	3.5	3.6	19.9 ± 3.0		
Ca (g/kg)	44.8	152.9	21.0	59.7 ± 12.0		
Cr (mg/kg)	9.8	5.4	8.8	13.4 ± 3.5	15.99 ± 0.04	
Cu (mg/kg)	12.6	5.3	17.3	38.2 ± 6.7	58.55 ± 0.08	<300
Ni (mg/kg)	4.6	4.0	7.9	9.3 ± 2.4	11.04 ± 0.04	<50
Pb (mg/kg)	<2.0	<2.0	<2.0	6.3 ± 2.9	10.05 ± 0.12	<120
Zn (mg/kg)	75.2	54.7	109.8	217 ± 46	289.74 ± 0.67	<7800
Al (g/kg)	27.7	0.6	37.2	1.5 ± 0.5		
Fe (g/kg)	1.5	1.1	1.8	0.7 ± 0.1		
Co (mg/kg)	0.8	0.3	0.7	0.9 ± 0.2		
Mo (mg/kg)	2.2	0.5	2.1	18.4 ± 3.6		
Mn (mg/kg)	55.1	28.2	80.7	28.2 ± 6.8		
Cd (mg/kg)					0.11 ± 0.001	<1.5
Hg (mg/kg)					0.08 ± 0.02	<1

DM = dry matter, OM = organic matter, TN = total nitrogen, TP = total phosphorus, TC = total carbon, n.a. = not available.

[a] Median values are presented.

[b] The requirements of EU solid bio-based fertiliser with more than one macronutrients (EC, 2019).

hygienized with a high Ca/P ratio. Therefore, more agronomic trials are needed on the fertilising effect of N and P of different DPS relative to mineral FEV to optimise DPS utilization.

5. Potential contaminants in DPS

A number of potentially harmful compounds may enter the milk processing chain through various routes and ultimately accumulate in DPS (Fig. 2). Lactating animals are exposed to various chemicals, directly or indirectly, via the agricultural and veterinary practices on a farm (Fischer et al., 2011a). The active ingredient may be absorbed by animals, subsequently excrete into the milk, and eventually enter the waste stream through residual milk in the factory. In addition, some common contaminants such as dioxins and heavy metals are likely to be found in milk and dairy products, as they may enter and form incidentally during the production process (Fischer et al., 2011a). At present, there is limited information available on emerging contaminants in dairy processes. In this section, we list potential contaminants and their sources and fate in DPS.

5.1. *Antimicrobial drugs*

Antibiotics, including the *β*-lactams (penicillins, cephalosporins), tetracyclines, macrolides, aminoglycosides, quinolones and polymyxins, are the most frequently and commonly used antimicrobial drugs in dairy cattle management (Fischer et al., 2011a). They are widely administered to treat, control and prevent spread of diseases of dairy cows such as mastitis, laminitis, respiratory diseases, and metritis, and to enhance animal growth and feed efficiency (IDF (International Dairy Federation), 1997). All the administered antibiotics could enter the milk and subsequently transfer to other dairy products to some extent, depending on their physicochemical properties and ability to intact with the fat and protein (Giraldo et al., 2017). Adetunji (2011) found streptomycin, penicillin and tetracycline residues in soft cheese and yoghurt. Rama et al. (2017) indicated that amoxicillin, penicillin G and cloxacillin were the most frequently detected residues in the raw milk collected from six different major regions of Kosovo. Sniegocki et al. (2015) observed that chloramphenicol can be easily transferred from raw milk to commercial butter, white cheese, sour cream and whey, as this antibiotic accumulates in dairy products with high fat content. The antibiotic residues in the dairy products may eventually enter the waste stream, but current wastewater treatment technologies are unable to remove traces of antibiotics from wastewater (Phoon et al., 2020). Once added to soil, antibiotics affect the structure and function of soil microbial communities and induce phytotoxic effects on plant growth (Jechalke et al., 2014). Current antibiotic wastewater technologies including advanced oxidation processes (AOP), advanced treatment (adsorption and membrane) and biological treatment, have advantages (AOP can destroy the chemical structure of pollutants) and disadvantages (the pollutants were degraded in after AOP, but the toxicity remained) (Phoon et al., 2020). Hybrid technologies, involving several combinations of several technologies, are capable of removing antibiotics (Phoon et al., 2020).

5.2. *Hormones*

Endogenous hormones occur naturally in food of animal origin because animals can excrete steroid hormones. The amount excreted depends on age, state of health, diet, or pregnancy (Silva et al., 2012). Hormones are also used to promote growth, increase food production, medical treatment and improve reproductive performance, but the use of anabolic hormones in animal production is prohibited in the EU (EC, 1996; EC, 2003; IDF , 1997). Seventy-five percent of milk is produced predominantly by pregnant cows, which means that milk represents an important source of steroid hormones (Goyon et al., 2016). The natural hormone content of milk is typically between 40 and 500 μg/kg for the steroids (IDF , 1997). During the processing in the dairy plants, the residual hormones will enter the effluent through residual milk. In a WWTP, some hormones are removed through sorption to TSS and degradation, followed by removal of the excess sludge (Silva et al., 2012), which means that hormones may accumulate in the DPS.

5.3. *Pesticides*

Pesticides, including insecticides, herbicides, rodenticides and fungicides, applied in agriculture, have been shown to transfer to dairy animal bodies through feed and fodder (Rather et al., 2017). In addition, to protect the animals against disease from mites, ticks and insects, some

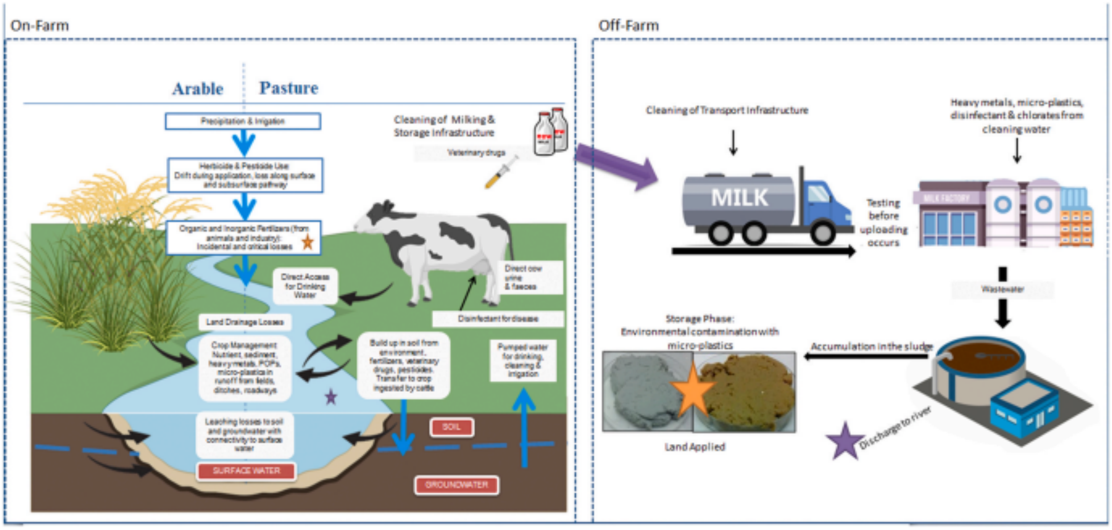

Fig. 2. The sources and fates of emerging contaminants in DPS.

pesticides are directly sprayed to the animals when they are housed. Animals will absorb pesticides orally, cutaneously, or via inhalation in such closed environments (Fischer et al., 2011a). Currently, common pesticides, including organophosphate, pyrethoids and carbamates, can be used on both routes and lead to the bioaccumulation in the dairy products (Akhtar and Ahad, 2017). The pesticides used in the cropping system and their metabolites will be lost to the environment via volatilization, aerial drift, runoff to surface water bodies, and leaching into groundwater basins (Wang et al., 2019), which can accumulate in the dairy animals or directly compromise drinking water used in the dairy factory. The residues of organochlorines and their metabolites also need to be considered. Although banned in many countries since the 1970s, residues still can be found in the environment due to their persistence and prolonged efficacy (Fischer et al., 2011a; Akhtar and Ahad, 2017). There is a vast list of pesticides used currently or in the past in agriculture with various levels of persistence in the soil, bedrock and water phases (McManus et al., 2017). This could have implications for grazing animals especially on heavy drained soils where, for example, 2-methyl-4-chlorophenoxyacetic acid (MCPA), which has a high solubility and low adsorption to soil matrix, is used to clear vegetation and has been found to have a much longer residence time in anaerobic waterlogged conditions (Morton et al., 2020).

From the US Food and Drug Administration data, dichlorodiphenyltrichloroethane (DDT) and its metabolites dichlorodiphenyldichloroethylene (DDE) and dieldrin, are the most commonly detected pesticides in foodstuff, including baked goods, fruit, vegetables, meat, poultry and dairy products (Schafer and Kegley, 2002). The OC pesticide, chlordane, has been found at a concentration of 1 ng/mL in raw milk samples (Fernandez-Alvarez et al., 2008). Golge et al. (2018) analysed 92 real dairy samples including raw milk, whole UHT (ultra-high-temperature) milk, Feta cheese and cream obtained from retail markets in Turkey, but none of the 167 pesticide residues were detected.

5.4. *Disinfectants*

Each procedure of the milk and dairy products process requires cleaning and disinfection to ensure removal of the bacteria and milk residues from all contact surfaces, including all processing equipment, transfer lines, tanks, trays, bins, blenders and conveyors (Cardador and Gallego, 2015). The most commonly used disinfectants are iodine-liberating agents, chlorine-containing substances, quaternary ammonium compounds, and hydrogen peroxide (Fischer et al., 2011a). A large amount of cleaning and disinfection agents enter dairy wastewater during the rinse-and-wash cycle of CIP system. Furthermore, using inadequately treated water to rinse and wash can be another source of contamination (McCarthy et al., 2018). Disinfectants are directly applied in the dairy wastewater to kill pathogens (e.g. faecal coliform and total coliform) during wastewater treatment (Akhlaghi et al., 2018). The residual of disinfectants could be either in their original state or as disinfection by-products (DBPs). Iodine sanitizers, usually as iodophors, are widely used in teat and skin disinfectants, filling/packaging machines, culture processing equipment, drop hoses, and hand dipping stations (Hladik et al., 2016). Iodinated DBPs are considered to be one of the most toxic DBPs, but have been tested less frequently than chlorine DBPs (Postigo and Zonja, 2019). Hladik et al. (2016) found trihalomethanes (THMs), including iodinated THMs, in the dairy wastewater and surface waters that receive dairy effluents (either directly from the dairy or through a WWTP).

Sanitation of water and equipment with chlorine-containing substances such as chlorine gas (Cl_2), dioxide (ClO_2), chlorhexidine and hypochlorite (ClO^-), remains common practice due to chlorine's bactericidal and oxidative properties (McCarthy et al., 2018). Chlorine reacts with any natural organic matter present in milk to form chlorine DBPs (Cardador and Gallego, 2015). Cardador and Gallego (2015) tested 84 milk and dairy products samples and found that 17 of them contained haloacetic acids (HAAs), the major class of non-volatile DBPs. The HAAs found in commercial samples can be attributed to contamination within the industrial processes like the washing of packages and equipment.

5.5. *Persistent organic pollutants (POPs)*

There are thousands of persistent organic pollutants (POPs) widespread in the environment. POPs tend to accumulate in the food chain because of their lipophilicity and low biodegradability (Jones and De Voogt, 1999). Since POPs occur ubiquitously, dairy animals are at danger from various sources of POPs, and these contaminants may transfer to the milk. In addition, some POPs such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins and furans, are common by-products or formed incidentally in industrial processes, and may subsequently enter the wastewater and sludge (Fischer et al., 2011b). PAHs are generally formed through a series of combustion processes occurring in industrial units. Boruszko (2017) detected 16 PAHs contents in three types of DPS and found 689 μg/kg dry matter (DM) in excess sludge, 95 μg/kg in post-flotation sludge, and 497.7 μg/kg DM in a mixture of excess and flotation sludge, which are considerably lower than the maximum permissible content of PAHs in biosolids (6 mg/kg DM) defined by EC (EC, 2000). A survey on 239 raw milk samples in France found that the average polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and PCBs concentrations were 0.33 pg toxic equivalent (TEQ)/g fat and 0.57 pg TEQ/g fat, respectively (Durand et al., 2008). Mamontova et al. (2007) found PCBs residues in milk and obtained a good correlation between PCB concentrations in milk and soil. Furans can be formed from the dehydration of sugars and would be expected to be found in dairy products that have been heated. Heaven et al. (2014) found three analogues of furan in the milk sample.

5.6. *Microplastics*

Plastic particles with diameters ranging from 0.1 μm to 5 mm are defined as "microplastics" and are a widespread anthropogenic pollutant in the environment with the extensive use of plastic (Phuong et al., 2016). Microplastics are mainly derived from synthetic fibres in clothing, industrial processes and personal care products, such as face cleaning soaps (Åström, 2016; Fendall and Sewell, 2009; Mahon et al., 2017). As an important food processing industry, the fate and sources of microplastics during the production process of dairy industry are largely unknown. The possible risks of milk contamination for microplastics may occur from cleaning equipment, the surrounding environment, as well as water supply conditions and inadequate handling of milk (Kutralam-Muniasamy et al., 2020). In addition, plastic-based packaging materials may lead to the microplastic contamination of milk. Kutralam-Muniasamy et al. (2020) collected 23 milk samples in Mexico and measured microplastics in the samples with an average of 6.5 ± 2.3 particles/L.

5.7. *Nano particles*

Nanotechnology, the designing and manufacturing of nano-scale (<100 nm) materials with specific chemical and physical properties (Kaegi et al., 2011), has been widely used in such applications as medicines, alternative energy, catalysts, and consumer products (Wang et al., 2017). Nanoparticles (NPs) primarily include silver, gold, copper, copper oxide, zinc oxide, titanium dioxide, manganese oxide, carbon nanotubes and magnetic matter (Wang et al., 2017). WWTPs are one of the most important pathways for NPs to enter the environment. The presence of NPs may have an effect on P removal and recovery (Chen et al., 2013).

6. STRUBIAS materials derived from DPS

Dairy factories produce large amount of DPS, which, on occasion, cannot be applied to land due to the limited nearby land bank for its application. This suitability may be driven by many factors such as soil type, crop type, weather conditions for trafficability, or farmer perception due to a lack on crop and sample specific FEV. Local oversupply of DPS leads to environmental issues including nutrient runoff, leaching, methane emissions, odour, and the accumulation of certain substances in soil through application over many years (Gascó et al., 2018; Kwapinska et al., 2018). Incidental runoff losses of nutrients and carbon from land application of DPS may also pose a risk to surface water quality deterioration. A recent study showed that edge of field-losses of NH_4–N and carbon from three types of DPS application was highest for Fe-rich DPS, whereas Ca–P-rich DPS showed highest dissolved reactive P losses but lowest losses of NH_4–N and carbon (Ashekuzzaman et al., 2020). Therefore, in the long term, there is a need to find alternative technologies to recover energy and nutrients from DPS. STRUBIAS manufacturing technologies has attracted attention and can potentially add value to DPS. The potential use, current problems and knowledge gaps of STRUBIAS products are investigated in this section (Table 5).

Table 5
The potential of DPS and its by-products application and current knowledge gaps.

Products	Potential Use	Current Problems	Current Scientific Knowledge Gaps
Bio-chemically treated activated sludge "AC"	As a grassland and arable organic fertiliser	Farmers need more fertiliser value to optimise application and maximise yield responses, odour and local oversupply	Full nutrient and emerging contaminant content characterisation, N–P–K fertiliser value for a variety of crops and soil types, gaseous emissions and long-term agronomic trials absent.
Lime treated DAF sludge "DAF"	As a grassland and arable organic fertiliser	Farmers need more fertiliser value to optimise application and maximise yield responses, odour and local oversupply. Decomposes quickly leading to fungus problem	Full nutrient and emerging contaminant content characterisation, N–P–K fertiliser value for a variety of crops and soil types, gaseous emissions and long term agronomic trials absent.
Sludge Ash	Phosphorus resource.	High heavy metal content	Need technology to remove heavy metals. Alternative uses.
Biochar	Energy production, carbon sequestration, organic soil amendment, absorbent for heavy metals	The impacts on soil and crops, the heavy metal and organic contaminants, the cost of production and transportation	The properties of chars and the mechanism of interaction between chars and soil, long term environmental risk
Pyrochar	Carbon sequestration, organic soil amendment, absorbent		Very few studies on pyrochar and hydrochar. More data are needed. What are suitable amendment rates and how often? Fertiliser value, the technology to remove heavy metals from feedstocks (ash and hydrochar) and optimise the P recovery
Hydrochar	Energy production, carbon sequestration, organic soil amendment, absorbent, bio-refinery.		
Struvite	Phosphate fertiliser	The technology of struvite precipitation	More research is needed on the purity of struvite.

6.1. *Struvite*

Struvite (magnesium ammonium phosphat hexahydrate, $MgNH_4PO_4.6H_2O$) is a P mineral that can be precipitated from aqueous waste streams by increasing the pH of wastewater and maintaining a stoichiometric PO_4^{3-} to Mg^{2+} molar ratio (Hertzberger et al., 2020). Struvite precipitate is normally formed in WWTPs during the anaerobic digestion process when significant levels of Mg occur in the wastewater (Booker et al., 1999). Occasionally, large amounts of struvite may form and deposit on the walls of the digesters and connecting pipes, which results in downtime, loss of hydraulic capacity and increased maintaining costs (Booker et al., 1999). However, struvite precipitation is an effective P recovery method. The pilot and operational facilities that manufacture struvite are commonly installed at municipal WWTPs, but are not frequently installed at food processing plants (Huygens et al., 2018). Struvite is an excellent fertiliser because it has similar fertiliser efficiency to common mineral P fertilisers such as single super phosphate and triple superphosphate (Johnston and Richards, 2003). Compared with traditional fertilisers, struvite has a high P_2O_5 content, and is an excellent slow release fertiliser that does not "burn" roots when over applied (Xu et al., 2012). The fertilising effect of the struvite precipitate on maize was investigated in a pot trial and the results obtained show that struvite can be an effective source of fertiliser (Uysal and Kuru, 2015). Struvite precipitation from different wastes like dairy, urine, swine manure, semiconductor wastes, sludge, and reject water from sludge thickening and dewatering process is also practised (Li et al., 2019; Ren et al., 2016). However, the chemical compositions of waste-recovered struvite are not always consistent with pure struvite (Hall et al., 2020). Furthermore, metal impurities such as Al, Fe, Ca and small amount of heavy metals can also precipitate along with the struvite (Li et al., 2019). Dairy waste including wastewater, DPS and other STRUBIAS co-products show a significant potential for P recovery in the form of struvite. Uysal and Kuru (2015) detected high N, P and Mg contents in struvite precipitate produced from dairy industry wastewater, while heavy metal concentrations were below detection limits. However, if the dairy wastewater is rich in Ca, the struvite crystallization rate and product quality might be affected and may require additional steps (e.g. calcium removal or step-by-step precipitation) as a pre-treatment process (Li et al., 2019). Chelating agents like ethylenediaminetetraacetic acid (EDTA) addition, sodium carbonate addition and CO_2 stripping are the feasible technologies to remove Ca in wastewater to enhance the purity of the obtained struvite (Hu et al., 2020; Zhang et al., 2010). Becker et al. (2019) reclaimed both N and P from hydrochar-derived sewage sludge and its process liquid via struvite precipitation. An acid leaching step removed phosphate from the hydrochar, while the process liquid arising from hydrothermal carbonization (HTC) was used as an NH_4 source for struvite precipitation. Xu et al. (2012) used an acid leaching method to extract P and produce struvite from sludge ash, which recovered more than 97% of P in sludge ashes.

To date, very few studies have investigated struvite precipitation from the dairy industry. The efficiency of P recovery and the precipitation technology needs to be further studied and optimised, as there are multiple factors that could potentially lead to inconsistency in the composition and speciation. In addition, research is needed to assess the toxicological compounds in the struvite because the contaminants in hydrochar and sludge ash might be simultaneously leached during P extraction.

6.2. *Char-based materials*

The term "char-based materials" is used here to replace 'biochar' in the STRUBIAS acronym, as they have different terms depending on the technology. Char-based materials obtained from the thermochemical conversion of biomass in an oxygen-depleted atmosphere are porous and carbonaceous, and are more stable and C-rich and less toxic than the feedstock (Atallah et al., 2020; Kambo and Dutta, 2015). Different thermochemical pre-treatment processes and conditions result in different final products. Pyrolysis is a prevailing thermal decomposition technology of OM (e.g. agricultural wastes, lignocellulosic biomss and sewage sludge) to convert biomass into valuable products like biochar, bio-oil and gas components at temperatures between 350 and 1000 °C in the absence of oxygen (Nanda et al., 2016; Ashekuzzaman et al., 2019b). Pyrolysed OM with a C content higher than 50% of DM are defined as biochar, otherwise, they are defined as pyrochar (EBC, 2012). HTC is, in contrast to pyrolysis, a wet conversion technique, degrading the OM content of sludge in the presence of water at a temperature range of 180–260 °C (Kambo and Dutta, 2015). Other than in pyrolysis, the HTC process does not require the drying of feedstock before and/or during the reaction (Malghani et al., 2013; Fakkaew et al., 2015). The HTC process produces a solid product, known as hydrochar, and a process liquid with high loads of small-chain organic acids, NH_4 and phosphate (Becker et al., 2019). It may therefore be more energetically efficient to convert wet biomass like DPS to hydrochar (Mau and Gross, 2018).

There are many functions of char-based materials including, but not limited to, energy production, agriculture, carbon sequestration, wastewater treatment and bio-refinery (Kambo and Dutta, 2015). The utility of a specific char-based material for any particular application depends on its inherent properties, which are mainly affected by their feedstock, pre-treatment method, and temperature (Amoah-Antwi et al., 2020). For energy production, hydrochar is a very suitable candidate as hydrochar shows considerable reduction in the ash content compared to that of raw feedstock and biochar produced via slow pyrolysis (Kambo and Dutta, 2015). In agriculture, the use of char-based material as a soil amendment is anticipated to improve chemical, physical and biological properties of soil and thereby crop productivity (Laird et al., 2010). Those rich in available nutrients and minerals and/or showing high water holding capacity could be better used as soil amendments to improve fertility (Graber et al., 2010). If char-based materials are used for C sequestration, it is necessary for them to have high environmental stability (Mašek et al., 2013). The stability of biochar in soil depends on several factors, especially the production method (Lehmann et al., 2009). Studies have rejected the potential of using hydrochar for carbon sequestration due to the low stability of hydrochar in soil (Berge et al., 2013; Eibisch et al., 2013). Biochar usually has a high specific surface area (SSA, >400 m^2/g) and more condensed polyaramatic structures, and hence is a good adsorbent for various contaminants (Amoah-Antwi et al., 2020; Kambo and Dutta, 2015). Hydrochar usually has very low SSA and porosity compared to biochar; however, due to the presence of oxygen-rich functional groups on its surface, the adsorption capacity of hydrochar is also high (Liu et al., 2010). The HTC process is promising in the field of pyrolysis of biomass for bioenergy production. The intermediate products includes 2,5-HMF, aldehydes (acetic, lactic, propenoic, levulinic, and formic acids), and other phenolic compounds generated during HTC can potentially be used for the manufacture of chemicals in the bio-refinery industry (Kambo and Dutta, 2015). DPS could be potential candidate for thermochemical treatment due to its low heavy metal content. Sadeghi et al. (2018) spread biochar derived from air-dried DPS over the surface of small-scale boxes filled with an erosion-prone soil and found that the biochar increased C, N, OM and C/N of the soil. In addition, they detected that biochar production significantly decreases the heavy metal, N, P and K contents, and increased the C and C/N ratio. Their study showed the potential of DPS-derived biochar to be an eco-friendly soil amendment and carbonaceous adsorbent. Ashekuzzaman et al. (2019b) studied pyrochars originating from two DPS types, i.e. activated sludge and DAF sludge, and used them as a carbonaceous adsorbent for P removal from wastewater. They found that the type, composition and the mineral composition (i.e. availability of Ca, Mg and Si) of DPS-derived pyrochar samples were associated with P removal process. Atallah et al. (2020) carried out batch HTC experiments using DAF sludge to investigate the effects of changing temperature, residence time and water-sludge ratio on the yield and quality of the hydrochar. They found that the production of hydrochar improved the characteristics of DPS, and an increase in reaction temperature, residence time and water-sludge ratio increased the hydrochar yield along with their energy and carbon content, and decreased the oxygen and volatile matter content.

Despite the benefits of char-based materials, there are several knowledge gaps with respect to the application of char-based materials derived from DPS. First of all, thermochemical treatments increase the risk of producing chars with other highly toxic compounds produced from high-temperature reactions such as PAHs, PCBs, dioxins, furans, and PCDD/Fs (Amoah-Antwi et al., 2020; Kambo and Dutta, 2015). Heavy metals present in the feedstock are most likely to remain and concentrate in the chars (Shackley et al., 2010). Therefore, careful analysis of feedstock and final products is necessary to avoid contamination in the soil. Second, char-based materials are complex, multi-functional materials that require improved mechanistic knowledge and understanding of its production, properties, impacts and interactions. The knowledge of char-based materials, especially hydrochar, derived from DPS is still in its early stages of development and all the aspects mentioned require additional research. Their benefits should be maximized through the mechanistic process understanding. Third, the cost of collecting of feedstocks, transportation, production and storage need to be properly assessed and managed.

6.3. *Ashes*

Ashes are characterized as fly ash or bottom ash, or a combination formed through the incineration of bio-based materials by oxidation (Huygens et al., 2018). They can be obtained from incineration plants which produce ash-based materials specifically for further agricultural use, or can be a production residue resulting from incineration of wastes or other production process (e.g. energy). Ash normally contains valuable plant macronutrients such as K, P, S, Ca and Mg (Brod et al., 2012; Haraldsen et al., 2011; Insam and Knapp, 2011), especially the amounts of P (13.7%–25.7% P_2O_5), which can be comparable to commercial superphosphate (Xu et al., 2012). However, the potential utilization of ashes as fertiliser is limited, since it is also inevitably enriched in heavy metals (Franz, 2008; Herzel et al., 2016). Sludge ash could be a secondary feedstock in the production of marketable phosphate fertiliser. So far, there have been a number of studies on the technologies to extract and recover P from sewage sludge ash. Nakagawa and Ohta (2019) used alkaline leaching technology to recover P as calcium hydroxyapatite from sewage sludge ash. Acid solutions like H_2SO_4, HCl, HNO_3, and H_3PO_4 are usually used for ash leaching to extract P (Biswas et al., 2009; Tan and Lagerkvist, 2011). Franz (2008) recovered P as fertiliser by adding lime water to precipitate calcium phosphates and other calcium compounds. Herzel et al. (2016) used a new thermochemical process for sewage sludge ash treatment, which transformed the phosphate-bearing mineral phases into plant available phosphates.

7. Conclusion and future research

Based on the EU's Farm to Fork Strategy, sustainable agriculture and organic farming will be encouraged in the future. DPS is recognised as a new organic fertiliser and a potential feedstock of STRUBIAS products. STRUBIAS products have potential commercial applications as both fertilisers (e.g. struvite), fertiliser components and soil amendments (e.g. chars). An important outcome of this review is that testing and publication of nutrient and metal data pertaining to DPS and DPS-derived STRUBIAS characteristics is not common. This is exasperated by the lack of testing and publication of data for other constituents such as heavy metals, pathogens, antimicrobial drugs, hormones, pesticides, disinfectants, POPs, microplastics and nano particles. These constituents, introduced during processing or treatment of the products, may be present at the land application stage. This is of particular concern for bioaccumulation in the soil and crops, with associated incidental losses in surface or near surface runoff to the aquatic environment. In addition the nutrient content and availability to plants differs across sludge and STRUBIAS product types due to many factors such as the type of dairy processing plant, wastewater treatment process and production technologies. Equally, the fertilizer equivalency value for both P and N is not known for all products and is not factored into application rates. This means that at farm scale neither agronomic nor environmental needs are being optimised. Future work should focus on these outcomes in long term field trials.

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.

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An examination of maximum legal application rates of dairy processing and associated STRUBIAS fertilising products in agriculture

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ABSTRACT

The dairy industry produces vast quantities of dairy processing sludge (DPS), which can be processed further to develop second generation products such as struvite, biochars and ashes (collectively known as STRUBIAS). These bio-based fertilizers have heterogeneous nutrient and metal contents, resulting in a range of possible application rates. To avoid nutrient losses to water or bioaccumulation of metals in soil or crops, it is important that rates applied to land are safe and adhere to the maximum legal application rates similar to inorganic fertilizers. This study collected and analysed nutrient and metal content of all major DPS (n = 84) and DPS-derived STRUBIAS products (n = 10), and created an application calculator in MS Excel™ to provide guidance on maximum legal application rates for ryegrass and spring wheat across plant available phosphorus (P) deficient soil to P-excess soil. The sample analysis showed that raw DPS and DPS-derived STRUBIAS have high P contents ranging from 10.1 to 122 g kg^{-1}. Nitrogen (N) in DPS was high, whereas N concentrations decreased in thermo-chemical STRUBIAS products (chars and ash) due to the high temperatures used in their formation. The heavy metal content of DPS and DPS-derived STRUBIAS was significantly lower than the EU imposed limits. Using the calculator, application rates of DPS and DPS-derived STRUBIAS materials (dry weight) ranged from 0 to 4.0 tonnes ha^{-1} y^{-1} for ryegrass and 0–4.5 tonnes ha^{-1} y^{-1} for spring wheat. The estimated heavy metal ingestion to soil annually by the application of the DPS and DPS-derived STRUBIAS products was lower than the EU guideline on soil metal accumulation. The calculator is adaptable for any bio-based fertilizer, soil and crop type, and future work should continue to characterise and incorporate new DPS and DPS-derived STRUBIAS products into the database presented in this paper. In addition, safe application rates pertaining to other regulated pollutants or emerging contaminants that may be identified in these products should be included. The fertilizer replacement value of these products, taken from long-term field studies, should be factored into application rates.

1. Introduction

The approach to sustainable nutrient use in agriculture is changing and there are ambitious new regulations incorporating "circular economy" objectives (EC , 2020a). In the European Union (EU) the "Farm to Fork Strategy" (EC , 2020a) aims to accelerate the transition from inorganic to organic sources of fertilisers within sustainable food and agriculture systems. One of the recommended practices is to encourage the recycling of critical nutrients (mainly nitrogen (N) and phosphorus (P)) from municipal, agricultural and industrial waste streams as fertilisers, which is important for the conservation of limited natural resources and the prevention of environmental pollution. As one of the largest agri-food sectors in Europe (Augère-Granier, 2018), the dairy industry consumes large volumes of water and generates wastewater (up to 10 L L^{-1} processed milk) that contains high concentrations of nutrients needed for crop growth (total nitrogen, TN: 14–830 mg L^{-1}; total phosphorus, TP: 9–280 mg L^{-1}; Erkan et al., 2018). The dairy waste stream, therefore, is a valuable resource for both N and P recovery.

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Dairy processing sludge (DPS) is a settled solid-liquid by-product, rich in N and P, that is generated from dairy waste streams during wastewater treatment (Ashekuzzaman et al., 2019a, 2019b). Approximately 3.8 million tonnes are generated annually in the EU, which is equivalent to about 155 million tonnes of milk production (EC , 2020b). It is classified as a biosolid (Pankakoski et al., 2000), meaning that it may be applied to land as a fertiliser in most countries. For example, a recent report showed that 63% of the DPS produced in Ireland is applied to pasture and arable land and 13.6% is used for composting (Ryan and Walsh, 2016). DPS can be categorised based on the lime and metal salt addition during wastewater treatment, since P is frequently associated with calcium (Ca), aluminium (Al) and iron (Fe) in poorly soluble complexes (Brod et al., 2015). These elements are known to fix plant available P into unavailable forms in soil.

The valorisation of DPS into more stable (e.g. pelletized) fertiliser products is the most likely pathway to market. Raw DPS can be further processed into struvite, biochar and incineration ashes, collectively referred to as STRUBIAS (Huygens et al., 2018), which are categorised as secondary raw material-based fertilising products (EC , 2019). STRUBIAS materials have potential to become "component materials categories" (CMC) in the EU Fertilising Products Regulation (EC , 2019). This means that STRUBIAS materials can be used to produce fertilising materials with different intended functions, including inorganic and organic fertilisers, liming materials, growing media, soil improvers, plant biostimulants, and fertilising product blends (Huygens et al., 2018). To open the EU Single Market for these bio-based fertilisers, the new EU regulation will provide strict rules on safety, quality and labelling requirements for all types of fertilisers and will introduce new limit values for contaminants in fertilisers like cadmium (Cd) (EC , 2019). The dairy waste stream, including DPS and dairy wastewater, is a potential candidate for STRUBIAS materials production due to its high P concentration and low heavy metal content.

At present few studies that have examined the nutrient and metal profiles of DPS (which vary across processing plant, type, and seasonally) and DPS-derived STUBIAS products (Ashekuzzaman et al., 2019a, 2019b). As DPS is categorised as biosolids according to current practices in the EU (Pankakoski et al., 2000), its application to land is prohibited in some countries such as Belgium, Switzerland and Romania due to concerns of bioaccumulation of toxic metals and/or emerging contaminants in soil and crops (Milieu, WRC, RPA, 2013a, 2013b, 2013c). There are also concerns that the processing of DPS into STRUBIAS products may introduce more metals, which could then cause problems for agricultural lands (Shi et al., 2021). Therefore, a thorough investigation and creation of a calculator that enables calculation of permissible application rates of these products in the context of EU soil and fertilizer regulations (Ulrich, 2019) is needed but lacking, despite the fact that such work has been completed for other wastes spread on grasslands e.g. sewage sludge biosolids and bone meal on low P index soils (Lucid et al., 2013). In Ireland, land is used for crops, grazing, silage and forestry. Grassland (pasture, hay and silage) is the dominant crop (80% of utilisable land) (O' Donnell et al., 2021). The production of grass silage and arable crops like wheat to feed cattle is common (Velthof et al., 2014). Both of these dominant crops receive DPS and are therefore used in the present study.

The objectives of the current study were to: (1) collect, collate and present a comprehensive overview of nutrient and metal composition of the main DPS and DPS-derived novel STRUBIAS product types (2) calculate the maximum legal application rates for DPS and DPS-derived STRUBIAS for ryegrass and wheat, and (3) calculate the equivalent application rates of heavy metals.

2. Materials and methods

2.1. Sample sources

A sample archive was collated consisting of 84 DPS and 14 DPS-derived STRUBIAS samples. Sixty-three DPS samples, collected from 2016 to 2018, originated from the study of Ashekuzzaman et al. (2019a), and 21 DPS samples were collected in 2019 and 2020 for the current study. All DPS samples were collected using plastic containers with screw top lids from 12 dairy processing plants in Ireland. The DPS samples were categorised into three types, depending on the chemical added (Table 1): (1) activated sludge aluminum-precipitated (Al-DPS, n = 54) (2) activated sludge iron-precipitated (Fe-DPS, n=9), and (3) lime-stabilised sludge calcium-precipitated (Ca-DPS, n = 21). The 14 STRUBIAS products were categorised into three types (Table 2): struvite (n = 3), chars (n = 6), and ash (n = 1).

For struvite, three types of magnesium ammonium phosphate (MAP or struvite) were precipitated from dairy processing wastewater. The struvite precipitation was completed in a stirred batch reactor equipped with a 1 L beaker, water bath with temperature (22 °C) regulation (PLWC 35S), and up-stirrer (CAT-100) with control settings for time (1 h) and stirring rate (60 rpm). Three types of struvites (MAP1, MAP2 and CaMAP; Table 2) were produced from dairy processing wastewater by varying the pH, Ca:P, Mg:P and NH_4^+:P (Numviyimana et al., 2020).

Six chars are included in this study. Three of them were produced by slow pyrolysis and are referred to as pyrochar. One (PC1; Table 2) was produced from a mixture of biological DPS and spruce wood chips at a pilot-scale facility (Kwapinska et al., 2019), while another two were produced using an Al-DPS at 450 °C (Al-PC2) and 700 °C (Al-PC3) for 1 h (Hu et al., in preparation, 2021). The other three chars were produced through a hydrothermal carbonisation (HTC) process and are referred to as hydrochar (HC). These were produced using a raw Fe-DPS sample collected from a dairy processing plant in Ireland. The Fe-DPS sample was introduced into the reactor liner with no additional water (Fe-HC1; Table 2) or placed inside a reactor vessel with the addition of 1% H_2SO_4 to achieve moisture contents of 85% (Fe-HC2) and 90% (Fe-HC3), respectively. The time needed to reach the set point temperature (200 °C) of the reaction was around 3 h for Fe-HC1, and around 26 min for Fe-HC2 and Fe-HC3. Once the set point was reached, the stirrer was initiated at 25 rpm and 36 rpm for 2 h. The solid HC separated from the liquid portion through filtration and dried in an oven at 105 °C for 24 h. PC1 was ashed in a laboratory furnace at 650 °C for 3 h (residence time) and cooled down to room temperature while still in the furnace. The generated ash (A1; Table 2) was ground by mortar and pestle.

2.2. Sample analysis

All the raw DPS samples were stored in a cold room at 4 °C before analysis for dry matter (DM), organic matter (OM) and pH. The STRUBIAS samples were stored at room temperature and DPS were freeze dried at −55 °C for 48 h (ScanVac CoolSafe 55–9 Pro), before being pulverized in a mixer mill (Retsch MM200) with a vibrational frequency of 25 Hz for 1 min. The resulting powdered samples were stored in sample tubes at room temperature for nutrient, trace metal and other elemental compositional analysis.

The DM and OM were determined using standard gravimetric method 2540 G (APHA, 2005), where about 15–20 g of raw DPS was dried for about 24 h at 105 °C in an oven, followed by ignition of the dried residue at 550 °C in a muffle furnace for 1 h. The pH was determined in a 1:2.5 (w/v) ratio of fresh DPS to deionized water solution (making up to 25 ml) by a Jenway 3510 pH meter after 1 h of mixing at 20 rpm by an end-to-end shaker (Ashekuzzaman et al., 2019a, 2019b). The concentrations of nutrients (P, potassium (K), magnesium (Mg), sulphur (S), sodium (Na), and Ca) and metals (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), Al, Fe, cobalt (Co), molybdenum (Mo) and manganese (Mn)) were determined 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 (USEPA, 1996). Samples were also analysed for total carbon (TC) and TN using a high temperature combustion method (LECO TruSpec CN analyser). The

Table 1

Dry matter, organic matter, pH and element concentration range in different types of DPS and comparison with regularity upper limit values for agricultural land application.

Sample Type	DM	pH	OM	TC	TN	NH$_4$–N	TP	TK	Mg	S	Ca	Fe	Al	Cu	Ni	Pb	Cd	Zn	Hg	Cr	As	Mo	Reference
	% of wt.		% of DM		g kg^{-1}									mg kg^{-1}									
Al-DPS (n = 54)	12.5 ± 3.2	7.1 ± 0.5	68.4 ± 8.1	32.6 ± 5.9	57.6 ± 8.8	3.8 ± 1.8	34.7 ± 11.1	7.4 ± 3.9	3.6 ± 1.7	5.5 ± 1.6	41.8 ± 20.0	1.4 ± 1.0	34.5 ± 16.6	2.4–34	<0.6–10.6	<2-4	<0.15–0.3	19–199.6	<0.1	2.5–19.6	<1.5	0.7–8.0	
Fe-DPS (n = 21)	20.1 ± 2.5	7.3 ± 0.4	52.1 ± 8.5	25.2 ± 4.6	45.6 ± 12.9	3.8 ± 1.2	40.7 ± 4.1	9.2 ± 4.1	2.9 ± 0.5	3.4 ± 0.3	78.1 ± 50.4	111.9 ± 37.3	0.8 ± 0.9	3.0–15.8	4.6–19.4	2.8-9.3	<0.15	92.6–180.6	<0.1	5.6–18.4	<1.5	<0.5–0.8	
Ca-DPS (n = 9)	21.8 ± 8.9	7.2 ± 0.7	47.2 ± 17.8	27.4 ± 13.3	30.8 ± 20.5	1.6 ± 1.2	52.8 ± 35.3	4.1 ± 2.2	4.9 ± 3.1	2.5 ± 1.4	155.9 ± 60.5	1.3 ± 1.0	0.8 ± 0.5	1.0–45.9	1.3–22.3	<2–9.6	<0.15–0.4	15.9–267.1	<0.1	3.2–17.2	<1.5	<0.5–22.5	
Regulations																							
EU limit														*1000–1750*	*300–400*	*750–1200*	*20–40*	*2500–4000*	*16–25*	-	-	–	EEC (1986)
Western Australia Grade C1														*100*	*60*	*150*	*3*	*200*	*1*	*100*	*20*	-	Western Australia, 2012
Western Australia Grade C2														*2500*	*270*	*420*	*20*	*2500*	*15*	*500*	*60*	-	
USA limit														*1500–4300*	*420*	*300–840*	*39–85*	*2800–7500*	*17–57*	-	*41–75*	*75*	US EPA (Environmental Protection Agency), 2007

DM = dry matter, OM = organic matter, TC = total carbon, TN = total nitrogen, TP = total phosphorus, TK = total potassium.

Al-DPS = aluminium-rich dairy processing sludge; Fe-DPS = iron-rich dairy processing sludge; Ca-DPS = calcium-rich dairy processing sludge.

Table 2

pH and element concentration range in DPS-derived STRUBIAS, comparison with regularity upper limit values for agricultural land application.

Sample Type	pH	TC	TN	NH$_4$–N	TP	TK	Mg	Na	S	Ca	Fe	Al	Cu	Ni	Pb	Cd	Zn	Hg	Cr	As	Mo
		% of DM	g kg^{-1}										mg kg^{-1}								
Struvite (n = 3)																					
MAP1		25.9	43.7	40.4	104.2	7.1	101.3	2.6	0.16	14.7	0.07	0.02	1.8	<0.6	<2	<0.15	30.1	<0.1	2.2	<1.5	<0.5
MAP2		38.8	29.4	15.4	80.2	7.5	62.2	8.8	0.46	34.5	0.17	0	0.21	<0.6	<2	<0.15	34.4	<0.1	2.8	<1.5	<0.5
CaMAP		31.6	11.2	0.33	47.0	6.5	18.8	31.7	0.62	66.9	0.39	0	0.38	<0.6	<2	<0.15	36.2	<0.1	3.3	<1.5	<0.5
Char (n = 6)																					
PC1		28.4	19.4	0.046	52.3	14.7	8.0	9.3	7.1	97.0	4.1	33.8	44.7	13.8	16.4	0.29	269.6	<0.1	25.7	2.2	5.4
Al-PC2		29.4	52.8	0.12	108.5	20.3	11.0	4.8	8.1	69.6	1.3	47.5	14.4	3.0	<2	<0.15	337.8	<0.1	10.2	<1.5	4.4
Al-PC3		28.0	41.1	0.002	113.0	26.1	14.7	6.0	3.4	83.6	1.1	59.6	20.4	5.8	<2	<0.15	478.3	<0.1	13.5	<1.5	5.4
Fe-HC1	6.9	22.6	37.5	0.026	78.9	13.5	3.7	2.8	3.2	68.0	177.3	8.0	47.8	7.6	5.9	<0.15	186.1	<0.1	6.5	<1.5	<0.5
Fe-HC2	7.9	18.4	29.4	0.031	85.4	8.5	3.7	1.8	12.8	72.0	199.7	8.5	6.1	9.4	5.9	0.25	185.9	–	6.8	<1.5	<0.5
Fe-HC3	7.7	21.2	36.5	0.025	79.9	12.6	3.5	2.6	8.2	65.7	183.4	7.8	5.4	9.1	5.3	<0.15	171.7	–	6.8	<1.5	<0.5
Ash ((n = 1)																					
A1	9.3	0.90	1.1	0.092	99.3	26.7	17.0	20.5	11.9	227.5	7.5	82.1	92.7	27.4	32.6	0.68	482.4	<0.1	41.2	4.1	11.1
Regulation																					
EU[a]													*300*	*50*	*120*	*1.5*	*800*	*1*	-	*40*	-

DM = dry matter, TC = total carbon, TN = total nitrogen, TP = total phosphorus, TK = total potassium.

MAP1, MAP2 and CaMAP were produced from dairy processing wastewater by varying the pH, Ca:P, Mg:P and NH4+:P (Numviyimana et al., 2020).

PC1 was produced from a mixture of biological DPS and spruce wood chips at a pilot-scale facility (Kwapinska et al., 2019).

Al-PC2 and Al-PC3 were produced by an aluminium-rich dairy processing sludge at 450 °C and 700 °C for an hour respectively.

Fe-HC1, Fe-HC2 and Fe-HC3 were produced by an iron-rich dairy processing sludge through a HTC process with no additional water or with addition of 1% H2SO4 to achieve moisture contents of 85% and 90%, respectively.

A1 was produced by PC1 in a laboratory furnace at 650 °C for 3 h.

[a] EU (2019).

mercury (Hg) analysis of two ash samples and three different samples, selected from the materials (Al-DPS, Fe-DPS, Ca DPS, struvite, and chars), was conducted by inductively coupled plasma atomic fluorescence spectroscopy (ICP-AFS). The mineral fraction (total oxidised N and ammonium nitrogen (NH_4–N)) of total N was analysed colorimetrically in the 0.1M HCl-extracted filtered solution using an Aquakem 600 Discrete Analyser. For extraction, 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.

2.3. *Calculation of maximum legal application rate ranges for DPS and STRUBIAS products*

The application rates of organic fertilisers and STRUBIAS products to agricultural land take cognisance of the limiting annual loading rate for metals and the nutrient requirements of plants. In the EU, it is common that fertilisers are applied to land based on their P content (e.g. S.I. EC, 2010 of http://www.environ.ie/en/Legislation/Environment/Water/FileDownLoad,25133,en.pdf ">2010 in Ireland), since applications based on the N requirement of a crop may result in excessive applications of P, which may cause nutrient losses to waters and, in the case of some biosolids, the build-up of heavy metals in the soil (Lucid et al., 2013). In Ireland, soil nutrient status is classified into index levels ranging from 1 to 4, depending on the quantity of the nutrient in the soil that is available to the crop (Table S1). The soil N index system is determined by the soil N supply status, while the plant available P is measured using Morgan's reagent (Teagasc, 2020). The application rate (in tonnes ha^{-1} y^{-1}) for the fertiliser products used was determined based on the P index level of the soil and the recommended N and P application rates for the target crop (such information is available in Ireland in the Teagasc Major and Micro Nutrient Advice for Productive Agricultural Crops Green book; Teagasc, 2020), the legal limits of metals, the dry matter content of the fertiliser, and its nutrient and metal concentration. The optimal application rates of DPS and STRUBIAS products for two different crops, ryegrass (*Lolium perenne* L.) and spring wheat (*Triticum aestivum* L.), were calculated using Microsoft Excel™ (Supplementary Material). Depending on the fertiliser application rates the annual equivalent loading rates of other elements including nutrients (N or P) and six EU regulated metals (Cd, Cu, Hg, Ni, Pb and Zn) are calculated (EEC, 1986).

3. Results and discussion

3.1. *Physicochemical composition*

The DPS and DPS-derived STRUBIAS materials are characterised for nutrients and metal composition and compared to EU legislation on metal concentrations in Tables 1 and 2 The three types of DPS examined were rich in the major plant nutrients, but they were not significant sources of K due to the elutriating effect of wastewater treatment on soluble components, similar to other biosolids (Rigby et al., 2016). The N and NH_4–N concentration was highest in the Al-DPS and lowest in the Ca-DPS. This may have been associated with lime addition, which causes losses of NH_3 and Ca–P precipitation (Ashekuzzaman et al., 2019a, 2019b). The concentrations of metals in the tested DPS samples were well below the EU regulatory guideline values (EEC, 1986). The concentrations of Cr, As and Mo are not currently regulated in the EU, but regulated elsewhere like western Australia and the USA (Western Australia, 2012; US EPA (Environmental Protection Agency), 2007), and were well below the upper limits of 75, 75 and 500 mg kg^{-1}, respectively. In Western Australia, there are three contamination levels for each contaminant in biosolids: Grade C1 is for the highest quality of biosolids, Grade C2 is middle quality, and Grade C3 represents the lowest quality. The parameters of DPS were well under the Grade C1 values, except the Zn content of two Ca-DPS (209.7 and 267.1 mg kg^{-1}, respectively).

Struvite is the preferred form of P recovery for fertiliser by chemical precipitation, considering its provision of P and N for plant nutrition (Daneshgar et al., 2018). The high P content of dairy processing wastewater makes it attractive for P recycling (Numviyimana et al., 2020). Despite the potential to recover nutrients by struvite precipitation, the chemical composition of the final product can vary widely and is not always consistent with pure struvite (Ahmed et al., 2018). MAP1 is produced under optimum conditions enhancing struvite crystallization, MAP2 is formed in conditions of both P removal and struvite production, and CaMAP is obtained in conditions of maximum P recovery with high dose of Ca salts (Numviyimana et al., 2020). Therefore, both MAP1 and MAP2 had higher P and N concentrations than CaMAP, as Ca^{2+} can compete with the NH_4^+ and Mg^{2+}, reducing struvite yield. Typically, Ca^{2+} promotes the precipitation of calcium phosphate ($Ca_3(PO_4)_2$) and hydroxyapatite ($Ca_{10}(PO_4)_6OH)_2$), which are compounds of very low solubility (Bauer et al., 2007).

Slow pyrolysis reduced the contents of total C, N and S in the resultant chars, as during thermal treatment significant amounts of feedstock-bound elements are volatilised in the form of CO, CO_2, NH_3, hydrocarbon compounds HCN and H_2S (Lu et al., 2012; Tian et al., 2002; Zhang et al., 2017). Furthermore, the higher the pyrolysis temperature, the lower the C and N in the biochars (Al-DPS, Al-HC1 and Al-HC2 in Table 2). The C contents in the Al-PC1 and Al-PC2 declined by 18.8% and 22.7% with a pyrolysis temperature at 450 °C and 700 °C, respectively, compared to the TC contents in their feedstock (Al-DPS), while the biochar TN contents decreased by 26.2% and 42.6% with two different temperatures. The emission of different N groups, such as the conversion to NH_3 from protein N at low temperatures (400–440 °C) and the conversion to HCN from pyridine at high temperatures (440–600 °C), caused TN decline (Wei et al., 2015). The pyrochars had higher TP contents compared to their feedstocks (mixture of biological DPS and woodchip, and Al-DPS; Table S2) and the TP in the biochars increased with increasing pyrolysis temperature, which means pyrolysis concentrated the P components in the biochars (Yuan et al., 2011). The concentration of total K increased relative to temperature because of the inorganic association of K with DPS (Hossain et al., 2011). Total concentration of the other elements, including Na, Ca, Fe and Mg, increased after pyrolysis treatment.

HTC is a relatively new technology to treat biomass residuals and a solid value-added product, HC, is produced. In comparison to traditional pyrolysis technology, HTC requires wet feedstock and therefore the DPS does not need to be dried prior to or during the process, saving substantial amounts of energy (Langone and Basso, 2020). It is noteworthy that, no matter how the pH of the experiment changes, the pH values of the HCs were neutral, similar to other studies (Liu et al., 2020; Wang et al., 2017). The concentration of C and N in the HCs decreased compared to their feedstock (Fe-DPS). However, the losses of C and N were much lower than pyrolysis, because pyrolysis resulted in the emission of gases at higher concentrations than HTC (Mau and Gross, 2018). HTC is conducted at high pressures with a closed reactor and all gases generated during the process are only emitted once the treatment has concluded. In addition, NH_3 is not emitted as a gas due to the low pH of the aqueous phase (Mau et al., 2016). Therefore, N in the HC might be plant available, and volatilised C and N can be dissolved in HTC liquor. The S content in Fe-HC1 decreased compared with the feedstock DPS, while S in Fe-HC2 and Fe-HC3 increased due to H_2SO_4 addition during the HTC progress of Fe-HC2 and Fe-HC3. The results show that HTC increased the content of some nutrients including P, Mg, Ca, Fe and Al, while decreasing the content of Na and K. This means that the nutrients in the feedstock are not completely concentrated in the HC, as part of them were in the HTC liquor. There are still considerable uncertainties about both the composition of HTC process waters and their potential valorisation. It is recommended that technology developers measure the composition of process waters, especially with respect to possible

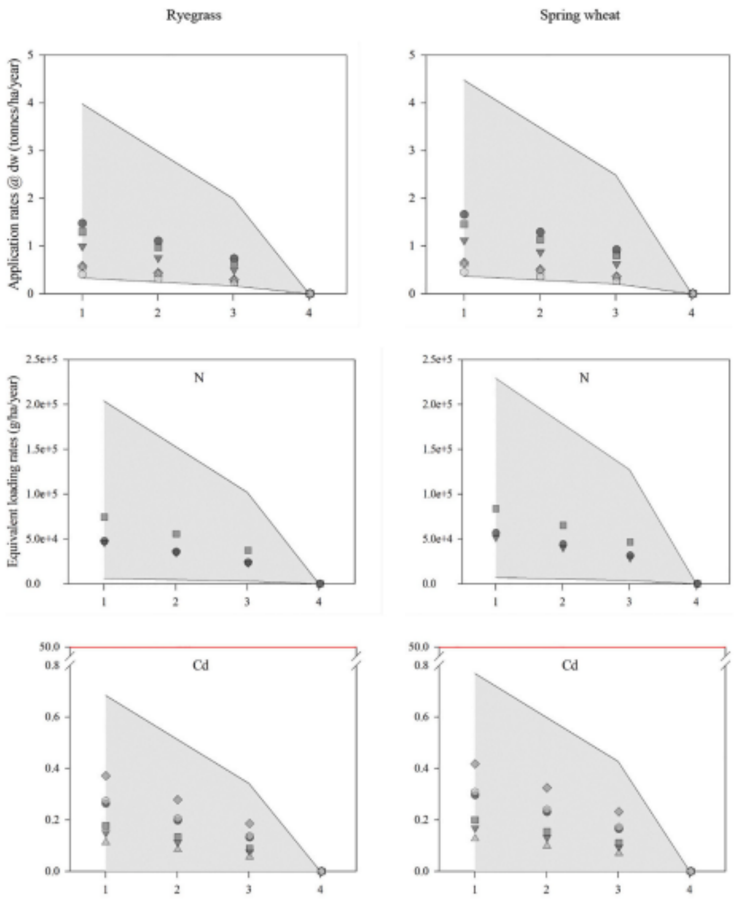

Fig. 1. The maximum legal application rates of three types of DPS and three types of DPS-derived STRUBIAS fertilising products calculated based on the soil P index and the equivalent loading rates of N and regulated metals. [circle icon] = Ca-DPS; [upside-down triangle] = Fe-DPS; [square icon] = Al-DPS; [diamond icon] = struvite; [triangle] = char; [hexagon] = ash; [red line] = maximum heavy metal addition to the land. Shaded area represents the maxima and minima for the application rates, across all products, at each soil P index. Since Hg results were all below the limits of detection, it is not included in this figure. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

application as fertilizer or for chemical recovery.

After the incineration of BC1 by oxidation, the contents of total C and N of ash significantly decreased, while all the other elements including nutrients and heavy metal concentration increased, which means they are concentrated in the ash.

Across three types of DPS-derived STRUBIAS products, the highest concentrations of Cu, Ni, Pb, Cd, Zn, Hg, and As were in ash and the lowest were in struvite. The total concentrations of Cu, Ni, Pb, Cd, Zn, Hg, and As in the chars and ash were higher than those in the feedstock DPS, but they were still under upper limits of the EU regulation for fertilisers (EC, 2019). It is likely that dissociation of organic compounds and some minerals, such as carbonates, caused by the pyrolysis temperature, contributed to an increase in heavy metal concentrations (Khanmohammadi et al., 2015).

3.2. *Application rates based on nutrients*

The high TP concentration in the DPS and DPS-derived STRUBIAS products examined in this study meant that maximum legal application rates for each soil P index were determined by the TP concentration of the material. The range of DPS and DPS-derived STRUBIAS application rates to ryegrass and spring wheat are shown in Fig. 1. Based on the TP content of different types of materials, application rates varied from 0 to 4.0 tonnes ha^{-1} y^{-1} on grassland and from 0 to 4.5 tonnes ha^{-1} y^{-1} on spring wheat.

The application rates do not consider the plant-available N and P in the DPS and DPS-derived STRUBIAS, which will affect crop uptake of nutrients. In comparison with chemical fertilisers, organic fertilisers provide less readily available nutrients which can become slowly available as the growing season progress (Chen, 2006). Some bio-based products might have poor nutrient availability, despite their relatively high P content. For example, Ashekuzzaman et al. (2021a, b) assessed P and N availability of Al-, Fe-, and Ca-DPS for crop yield and uptake in comparison to reference mineral fertilisers over 1 year at field-scale experiment. Their results showed that P availability differs significantly between Al- and Ca-DPS, and that mineral P fertiliser was initially much more readily available for plant uptake than DPS, since Al–P and Ca–P are less soluble than mineral P fertiliser. With regards to N availability, Ashekuzzaman et al. (2021b) also found a wide range of N-fertiliser equivalency values (FEV) among different DPS types (8%–54%).

Numviyimana et al. (2020) evaluated nutrient availability to plant for three struvites, MAP1, MAP2 and CaMAP (also used in the current study; Table 2), in an *in*-vitro study, in which the nutrients released in 2% citric acid with pH 6 were measured over 2 h. The results showed

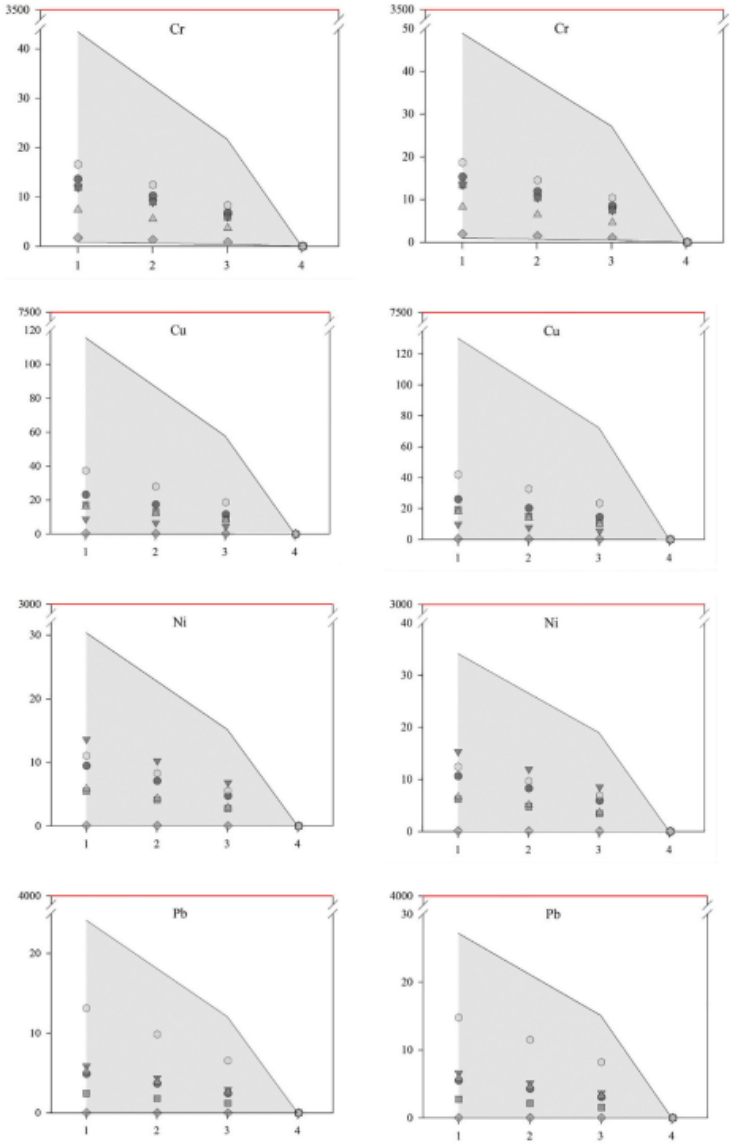

Fig. 1. (*continued*).

that although both MAP1 and MAP2 were characterized by higher P, Mg and N contents than CaMAP, MAP1 required a longer time to release N, P and Mg.

Biochar normally has low amounts of plant available N (Bridle and Pritchard, 2004). While losses of P during pyrolysis are negligible, P is converted into more stable, less available forms such as Mg or Ca minerals. Biochar, therefore, creates a more permanent nutrient pool for long-term nutrient uptake by crops (Frišták et al., 2018). In addition, NH_4–N and nitrate leaching reduce following biochar amendment (Yuan et al., 2016).

Ash from sludge incineration has higher P content (about 10%) than the original sludge before incineration (Lim and Kim, 2017; Liu et al., 2010). However, research shows that the bioavailability of P in the sludge ash is poor. The bioavailability of P can be estimated by the solubility of P in neutral ammonium citrate (P_{NAC}), mostly given as a fraction of the total P content (P_{NAC}-solubility) (Herzel et al., 2016). Krüger and Adam (2015) found that the mean PNAC-solubility of sewage sludge ash in Germany is very low (31% of total P). The P species of sludge ash are controlled by the wastewater treatment before incineration, which means P is mainly associated with Al, Fe or Ca (Nanzer et al., 2014). Therefore, direct application of sludge ash as a fertiliser is very rare due to low bioavailability of P and significant amount of heavy metals (Jeon and Kim, 2018).

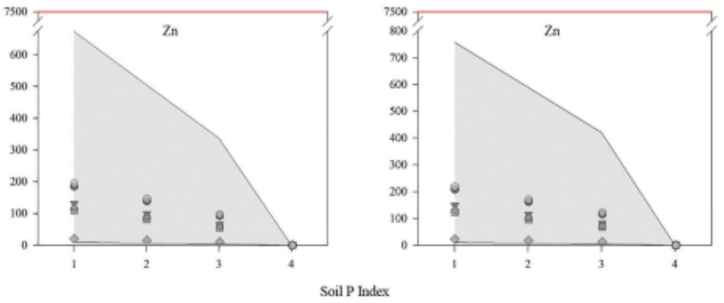

Fig. 1. (*continued*).

3.3. *Estimation of equivalent loading rates of heavy metals*

The EU sets average annual tolerance limits on heavy metal additions to soil over a 10-y period. These are (in g ha^{-1} y^{-1}) Cd: 50, Cr: 3500, Cu: 7500, Ni: 3000, Pb: 4000, Zn: 7500 and Hg: 100 (Fehily Timoney and Company, 1999). The loading rates of six EU regulated heavy metals were determined based on the application rates of P in the DPS and DPS-derived STRUBIAS (Fig. 1). All results show that application rates were low and considered safe in terms of bioaccumulation in soil and crops.

Struvite has the lowest heavy metal content of all products included in Table 2. Many studies describe struvite as a slow-release fertiliser for agricultural applications, which is not highly soluble and therefore not readily lost along surface runoff pathways to waters (Cieślik and Konieczka, 2017; Yetilmezsoy et al., 2017). The production of struvite also reduces the mass of the original substrate through the loss of OM and moisture (Hall et al., 2020; Kim et al., 2009). Therefore, struvite precipitation from DPS offers a relatively effective and environmental-friendly way to recover excess nutrients from wastes.

Although themo-chemical treatments including pyrolysis, HTC and incineration, increased heavy metal concentration, most of the heavy metals existed in the oxidisable and residual forms, especially when pyrolysed at 600 °C, resulting in a significant reduction in their bioavailability, leading to a very low environmental risk of chars and ash (Jin et al., 2016). However, if ash were directly applied to land, further processing to remove contaminants would still be needed.

3.4. *Future research needs*

Future research should focus on establishing the N-FEV and P-FEV of DPS and DPS-derived STRUBIAS products using pot and field trials. For example, the calculated application rates in this study do not consider the N and P availability of these products, which are more indicative of their performance as fertiliser replacements. Completion and incorporation of such research into the calculator for all DPS and DPS-derived STRUBIAS product and crop types would lead to more accurate incorporation of bio-based fertilizers into nutrient management planning. In addition, the application rates used in this study are regulated by guidance in Ireland, based on fixed nutrient application norms. Models that predict future P yields should represent a balance between P input and outputs in the field, which would lead to more efficient DPS and DPS-derived STRUBIAS application. Such a model has been completed for manure applications to both grassland and arable lands (Mollenhorst et al., 2020) leading to decreased P losses in waters where applied. The evolution of wastewater treatment techniques employed at dairy processing sites endeavours to follow advances in the treatment of human wastewater. From an economic perspective, there is a need to move away from dosing P-rich waste streams with metal salts towards biological P removal (Kolev Slavov, 2017). Such treatment will replace the need for metal flocculants to remove P, but will inevitably produce new sludge streams that will need to be characterised in terms of their FEV, nutrient and metal content.

Heavy metal and other emerging contaminants, present in some DPS or introduced due to the production and DPS-derived STRUBIAS products, need further review and characterisation. Indeed, the bioaccumulation of contaminants in soil and crops associated with land application of bio-based fertilizers needs investigation using long-term field trials since the accumulation of contaminants in soil, following repeated applications of these products, may be problematic.

The calculator created in this study should be developed into an online or phone application to guide growers, contractors, farmers and processing plant operators, as part of on-going nutrient management planning.

4. Conclusions

A total of 84 DPS and 14 DPS-derived STRUBIAS products were examined for their safe agricultural land application to comply with regulatory requirement for application rates and soil metal contamination from bio-based fertiliser application. All products tested had high P. Nitrogen in DPS was high, but N concentrations were low in the thermo-chemical STRUBIAS products. The heavy metal content of DPS and DPS-derived STRUBIAS tested were all lower than EU imposed limits and presented no problems regarding application rates. The calculated DPS and DPS-derived STRUBIAS maximum legal application rates, based on nutrients for ryegrass and wheat, were 0–4.0 tonnes ha^{-1} y^{-1} and 0–4.5 tonnes ha^{-1} y^{-1}, respectively. Future research should incorporate the FEV of DPS and DPS-derived STRUBIAS products into nutrient management planning. New wastewater treatment processes will lead to new DPS and STRUBIAS products, which will require analysis in long-term field trials.

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.

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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.2021.113880.

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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.,

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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)).

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

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

where $\mathrm{EQ}_{\mathrm{mineral\ N\ or\ P\ fertiliser\ rate}}$ is the equivalent amount of mineral N or P fertiliser that gives the same reference response compared to DPS, and $\mathrm{N}_{\mathrm{applied}}$ or $\mathrm{P}_{\mathrm{applied}}$ is the application rate of N or P in the DPS (Ashekuzzaman et al., 2021b). $\mathrm{EQ}_{\mathrm{mineral\ N\ or\ P\ fertiliser\ rate}}$ 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 $\mathrm{uptake}_{\mathrm{Treatment}}$ or P $\mathrm{uptake}_{\mathrm{Treatment}}$) and unfertilised plots (N $\mathrm{uptake}_{\mathrm{Control}}$ or P $\mathrm{uptake}_{\mathrm{Control}}$) (Murphy et al., 2013) (Eqns. (3) and (4)). MFE is the ratio of the apparent nutrient recovery of organic residues ($\mathrm{ANR}_{\mathrm{Treatment}}$ or $\mathrm{APR}_{\mathrm{Treatment}}$) 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).

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

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

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

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

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 ($\mathrm{NH_4}$–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 ($\mathrm{NO_2}$–N) and $\mathrm{NH_4}$–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 ($\mathrm{NO_3}$–N) was calculated by subtracting the concentration of $\mathrm{NO_2}$–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 $\pm$ 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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Appendix B

Appendix B. Guidelines on using the safe application rate calculator.

The calculator was developed to determine the optimal application rates of DPS and STRUBIAS products for ryegrass and spring wheat. This calculator can be developed further for other crops and modified easily as more EU regulations pertaining to metals or emerging contaminants emerge.

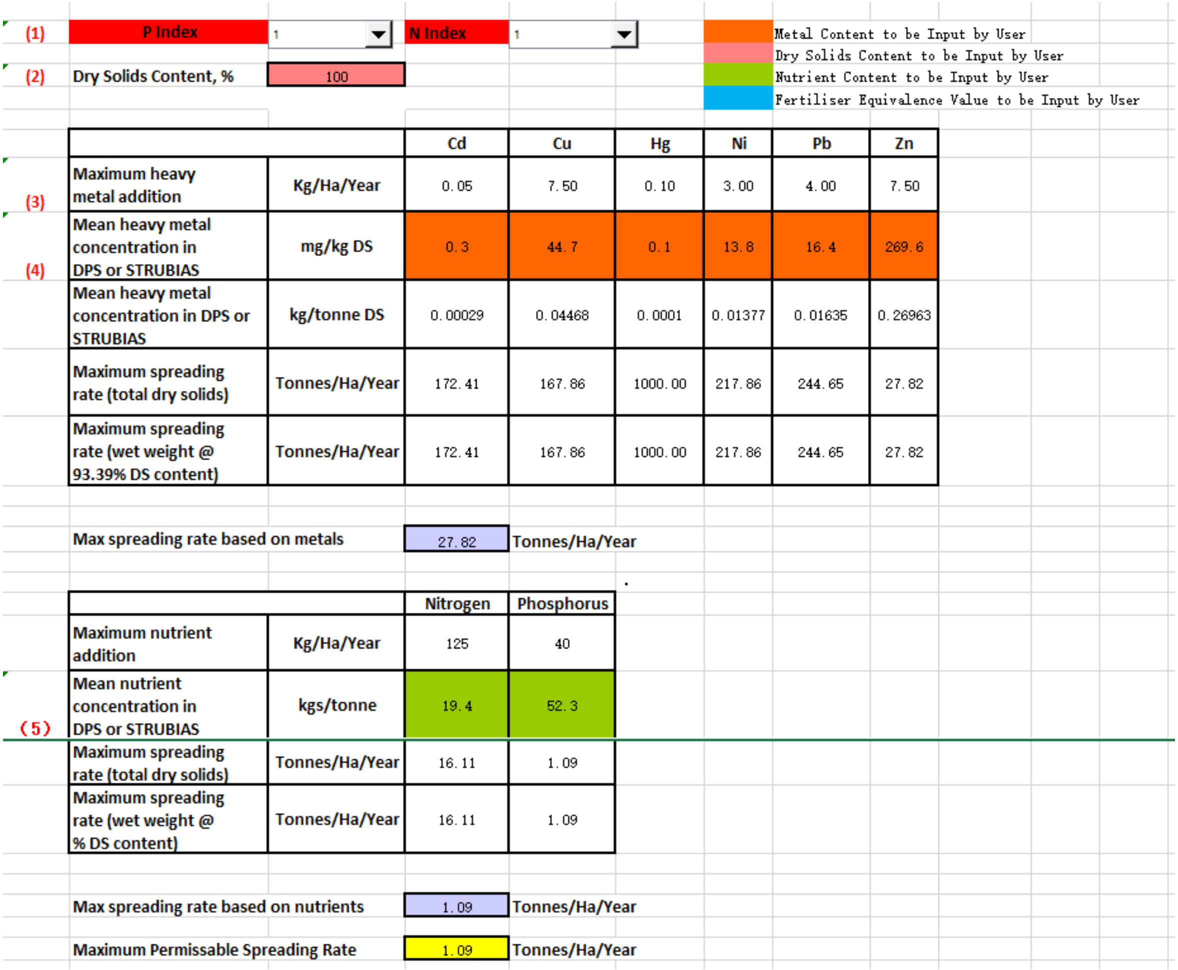
Figure 1 shows a suggested layout for the input of data to determine the maximum application rate to be land applied. The optimal amount of biochar to be applied to a soil for the growth of ryegrass was used as an example.

STEP1: The maximum nutrient loading rate is determined based on the P and N index of the soil, any combination of which can be specified by a drop-down function in the 'data' menu of Excel ('1' in Figure).

STEP2: The dry solids content of the products is inputted into the matrix ('2' in Figure). This rate may be adjusted to account for the dry solids content (DSC) of the media.

STEP3: The maximum permissible rate of heavy metal addition (kg ha-1 y -1) is entered in the spreadsheet ('3' in Figure). The metal content (mg kg-1 DS) of DPS or DPS derived STRUBIAS products is then inputted into the matrix ('4' in Figure).

STEP4: The nutrients content (kgs t-1) is inputted into the matrix ('5' in Figure).



(1) P Index 1 N Index 1

(2) Dry Solids Content, % 100

🟧 Metal Content to be Input by User
🟥 Dry Solids Content to be Input by User
🟩 Nutrient Content to be Input by User
🟦 Fertiliser Equivalence Value to be Input by User

			Cd	Cu	Hg	Ni	Pb	Zn
(3)	Maximum heavy metal addition	Kg/Ha/Year	0.05	7.50	0.10	3.00	4.00	7.50
(4)	Mean heavy metal concentration in DPS or STRUBIAS	mg/kg DS	0.3	44.7	0.1	13.8	16.4	269.6
	Mean heavy metal concentration in DPS or STRUBIAS	kg/tonne DS	0.00029	0.04468	0.0001	0.01377	0.01635	0.26963
	Maximum spreading rate (total dry solids)	Tonnes/Ha/Year	172.41	167.86	1000.00	217.86	244.65	27.82
	Maximum spreading rate (wet weight @ 93.39% DS content)	Tonnes/Ha/Year	172.41	167.86	1000.00	217.86	244.65	27.82

Max spreading rate based on metals 27.82 Tonnes/Ha/Year

			Nitrogen	Phosphorus
	Maximum nutrient addition	Kg/Ha/Year	125	40
(5)	Mean nutrient concentration in DPS or STRUBIAS	kgs/tonne	19.4	52.3
	Maximum spreading rate (total dry solids)	Tonnes/Ha/Year	16.11	1.09
	Maximum spreading rate (wet weight @ % DS content)	Tonnes/Ha/Year	16.11	1.09

Max spreading rate based on nutrients 1.09 Tonnes/Ha/Year

Maximum Permissable Spreading Rate 1.09 Tonnes/Ha/Year

Figure. Screen-grab of the Excel program used to calculate the maximum legal application rate

STEP5: the maximum spreading rate based on nutrients and the maximum permissible spreading rate are given as outputs.