



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

W. Shi^{a,b}, O. Fenton^{a,b,*}, S.M. Ashekuzzaman^a, K. Daly^a, J.J. Leahy^c, N. Khalaf^c, Y. Hu^d, K. Chojnacka^e, C. Numviyimana^e, M.G. Healy^b

^a Teagasc, Environmental Research Centre, Johnstown Castle, Co, Wexford, Ireland

^b Civil Engineering and Ryan Institute, College of Science and Engineering, National University of Ireland Galway, Galway, Ireland

^c Chemical and Environmental Science, University of Limerick, Limerick, Ireland

^d Aarhus University, Faculty of Technical Sciences, Department of Engineering, Finlandsgade 12, 8200 Aarhus N, Denmark

^e Department of Advanced Material Technology, Faculty of Chemistry, Wrocław University of Science and Technology, ul. M. Smoluchowskiego 25, Wrocław, 50-372, Poland

ARTICLE INFO

Keywords:

Agriculture
Dairy processing waste
Bio-based fertilisers
Application calculator

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 thermochemical 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.

* Corresponding author. Teagasc, Environmental Research Centre, Johnstown Castle, Co, Wexford, Ireland.
E-mail address: owen.fenton@teagasc.ie (O. Fenton).

<https://doi.org/10.1016/j.jenvman.2021.113880>

Received 29 July 2021; Received in revised form 21 September 2021; Accepted 28 September 2021

Available online 9 October 2021

0301-4797/© 2021 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

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 (Ashkuzzaman 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 STRUBIAS products (Ashkuzzaman 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 Ashkuzzaman 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 NH₄⁺: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% H₂SO₄ 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 (Ashkuzzaman 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	Zn	Hg	Cr	As	Mo	Reference	
	% 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 ± 2.0	41.8 ± 1.0	1.4 ± 1.0	34.5 ± 16.6	2.4 ± 2.4	<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 20–40 100 60 200 1 100 20 - - EEC (1986)																					
Western Australia	2500 270 420 20 2500 15 500 60 - - Western Australia, 2012																					
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	
	mg kg ⁻¹																					
Strawite (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	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	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	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	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 (NH₄-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 NH₄-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 NH₃ and Ca-P precipitation (Ashkuzzaman 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 Ca²⁺ can compete with the NH₄⁺ and Mg²⁺, reducing struvite yield. Typically, Ca²⁺ promotes the precipitation of calcium phosphate (Ca₃(PO₄)₂) and hydroxyapatite (Ca₁₀(PO₄)₆(OH)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, CO₂, NH₃, hydrocarbon compounds HCN and H₂S (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 NH₃ 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, NH₃ 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 H₂SO₄ addition during the HTC process 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

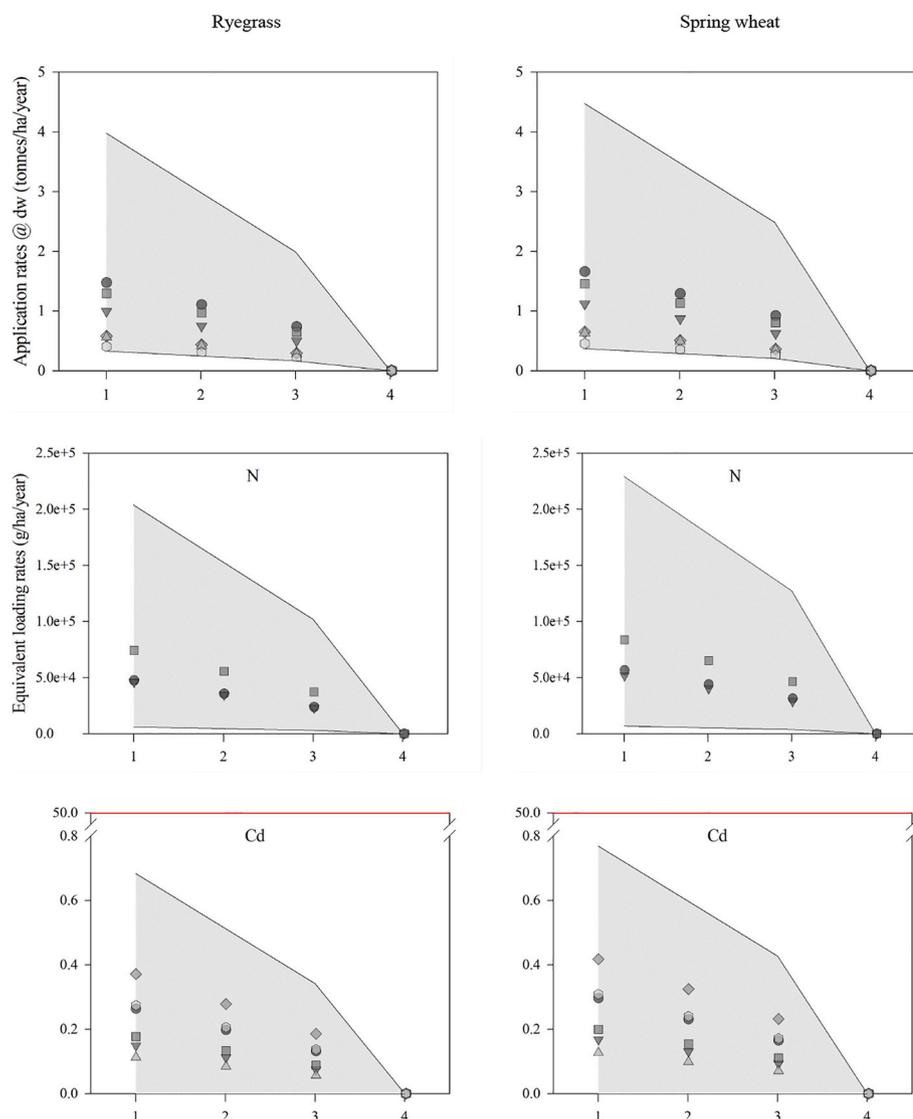


Fig. 1. The maximum legal application rates of three types of DPS and three types of DPS-derived STRUBIAS fertilising products calculated based on the soil P index and the equivalent loading rates of N and regulated metals. [circle icon] = Ca-DPS; [upside-down triangle] = Fe-DPS; [square icon] = Al-DPS; [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 BCI 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 $\text{ha}^{-1} \text{y}^{-1}$ on grassland and from 0 to 4.5 tonnes $\text{ha}^{-1} \text{y}^{-1}$ 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

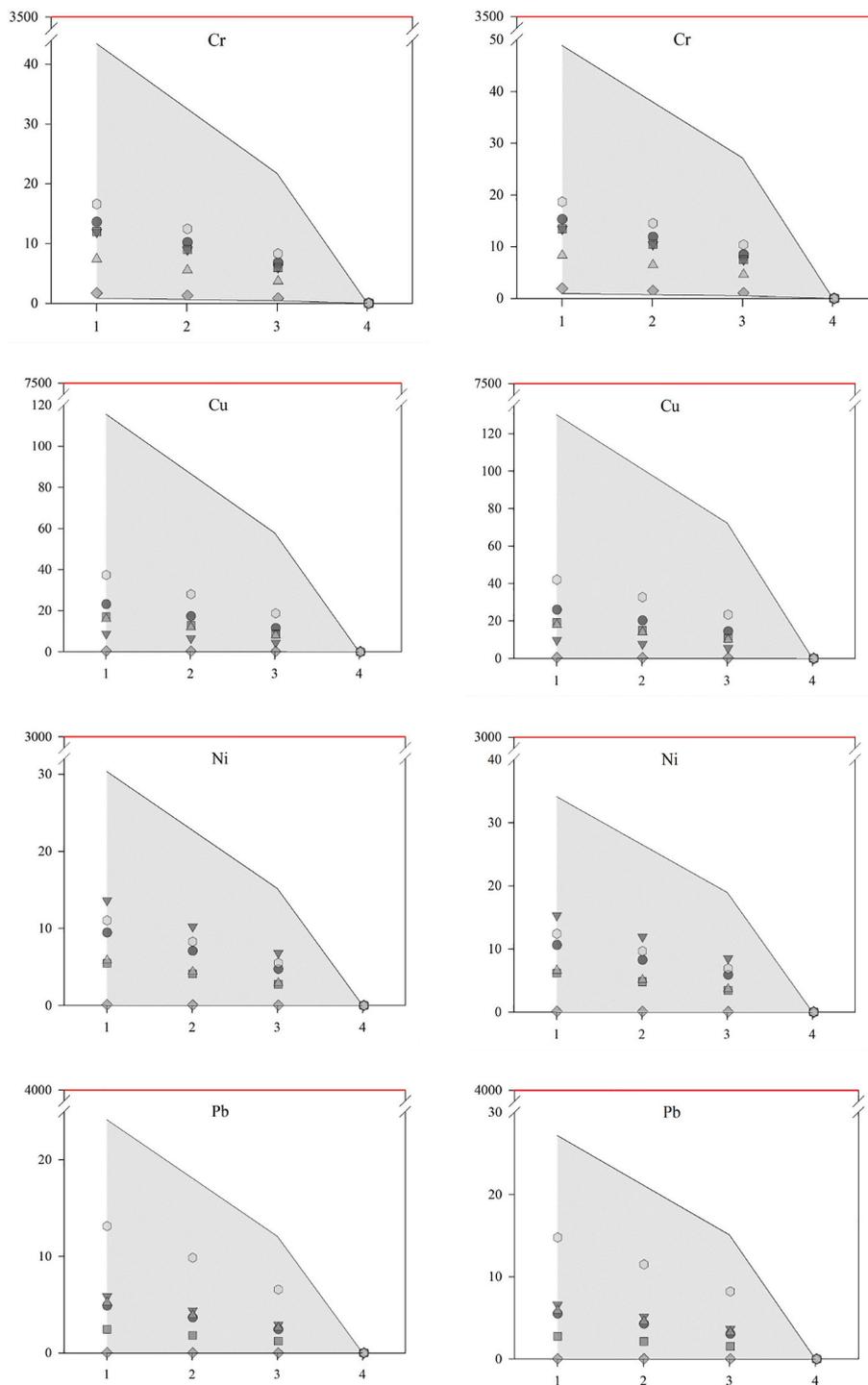


Fig. 1. (continued).

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 (Frísták et al., 2018). In addition, $\text{NH}_4\text{-N}$ 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 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, 2018).

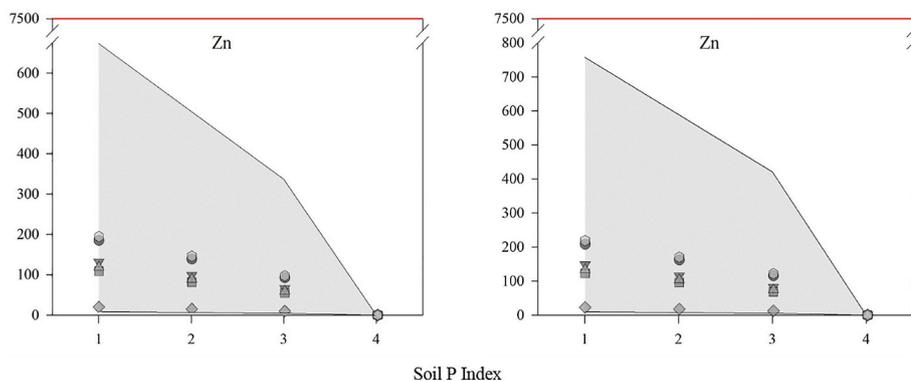


Fig. 1. (continued).

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 $\text{g ha}^{-1} \text{y}^{-1}$) 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 (Cieřlik 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 thermo-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 bio-accumulation 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 $\text{ha}^{-1} \text{y}^{-1}$ and 0–4.5 tonnes $\text{ha}^{-1} \text{y}^{-1}$, 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.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 814258.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2021.113880>.

Credit author statement

W. Shi: Conceptualization, Methodology, Writing – original draft. **O. Fenton:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition. **S.M. Ashekuzzaman,** Conceptualization, Methodology, Writing – review & editing, Supervision. **K. Daly,** Conceptualization, Methodology, Writing – review & editing, Supervision. **J.J. Leahy,** Funding acquisition. **N. Khalaf,** Resources, Data curation. **Y. Hu,** Resources, Data curation. **K. Chojnacka,** Resources, Data curation. **C. Numviyimana,** Resources, Data curation. **M.G. Healy,** Conceptualization, Methodology, Writing – review & editing, Supervision.

References

- APHA, 2005. Standard Methods for the Examination of Water and Wastewater, twenty-first ed. American Public Health Association, Washington DC, USA.
- Ashekuzzaman, S.M., Forrestral, P., Richards, K., Fenton, O., 2019a. Dairy industry derived wastewater treatment sludge: generation, type and characterization of nutrients and metals for agricultural reuse. *J. Clean. Prod.* 230, 1266–1275.
- Ashekuzzaman, S.M., Kwapinska, M., Leahy, J.J., Richards, K., Fenton, O., 2019b. Novel use of dairy processing sludge derived pyrogenic char (DPS-PC) to remove phosphorus in discharge effluents. *Waste Biomass Valorization* 11, 1453–1465.
- Ashekuzzaman, S.M., Forrestral, P., Richards, K.G., Daly, K., Fenton, O., 2021a. Grassland phosphorus and nitrogen fertilizer replacement value of dairy processing dewatered sludge. *Sustain. Prod. Consum.* 25, 363–373.
- Ashekuzzaman, S.M., Fenton, O., Meers, E., Forrestral, P.J., 2021b. Differing phosphorus crop availability of aluminium and calcium precipitated dairy processing sludge potential recycled alternatives to mineral phosphorus fertiliser. *Agron* 11 (3), 427.
- Bridle, T.R., Pritchard, D., 2004. Energy and nutrient recovery from sewage sludge via pyrolysis. *Water Sci. Technol.* Nov 50 (9), 169–175.
- Cieslik, B., Konieczka, P., 2017. A review of phosphorus recovery methods at various steps of wastewater treatment and sewage sludge management. The concept of “no solid waste generation” and analytical methods. *J. Clean. Prod.* 142, 1728–1740.
- EC, 2010. Statutory Instrument S.I. No. 610 of 2010, 2010. European Community. European Communities (Good Agricultural Practice for Protection of Waters) Regulations. Available online: <http://www.irishstatutebook.ie/eli/2010/si/610/ma/de/en/pdf>.
- EC (European Commission), 2019. Regulation of the European Parliament and of the Council Laying Down Rules on the Making Available on the Market of EU Fertilising Products and Amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and Repealing Regulation (EC) No 2003/2003. Available online: <https://data.consilium.europa.eu/doc/document/PE-76-2018-INIT/en/pdf>.
- EC (European Commission), 2020a. Farm to Fork Strategy: for a fair, healthy and environmentally-friendly food system. Available online: https://ec.europa.eu/food/sites/food/files/safety/docs/f2f_action-plan_2020_strategy-info_en.pdf.
- EC (European Commission), 2020b. Milk and dairy products. Available online: https://ec.europa.eu/info/food-farming-fisheries/animals-and-animal-products/animal-products/milk-and-dairy-products_en#:~:text=Total%20EU%20milk%20production%20is,yield%20per%20cow%20has%20improved (accessed on 27 November 2020).
- EEC, 1986. Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC). Available online: http://www.efma.org/PRODUCT-STEWARDSHIP-PROGRAM-10/images/86278_EEC.pdf (accessed 15.04.15).
- EPA (Environmental Protection Agency), 2007. Biological Nutrient Removal Processes and Costs. <https://doi.org/10.1017/CBO9781107415324.004>.
- Erkan, H.S., Gunalp, G., Engin, G.O., 2018. Application of submerged membrane bioreactor technology for the treatment of high strength dairy wastewater. *Braz. J. Chem. Eng.* 35, 91–100.
- Frišták, V., Pipiška, M., Soja, G., 2018. Pyrolysis treatment of sewage sludge: a promising way to produce phosphorus fertilizer. *J. Clean. Prod.* 172, 1772–1778.
- Herzel, H., Krüger, O., Hermann, L., Adam, C., 2016. Sewage sludge ash—a promising secondary phosphorus source for fertilizer production. *Sci. Total Environ.* 542, 1136–1143.
- Hossain, M.K., Strezov, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *J. Environ. Manag.* 92 (1), 223–228.
- 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 Fertilizer Regulation. Circular Economy and Industrial Leadership Unit, Directorate B-growth and Innovation.
- Jeon, S., Kim, D.J., 2018. Enhanced phosphorus bioavailability and heavy metal removal from sewage sludge ash through thermochemical treatment with chlorine donors. *J. Ind. Eng. Chem.* 58, 216–221.
- Jin, J., Li, Y., Zhang, J., Wu, S., Cao, Y., Liang, P., Zhang, J., Wong, M.H., Wang, M., Shan, S., Christie, P., 2016. Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge. *J. Hazard Mater.* 320, 417–426.
- Khanmohammadi, Z., Afyuni, M., Mosaddeghi, M.R., 2015. Effect of pyrolysis temperature on chemical and physical properties of sewage sludge biochar. *Waste Manag. Res.* 33 (3), 275–283.
- Kolev Slavov, A., 2017. General characteristics and treatment possibilities of dairy wastewater-A review. *Food Technol. Biotechnol.* 55 (1), 14–28.
- Krüger, O., Adam, C., 2015. Recovery potential of German sewage sludge ash. *Waste Manag.* 45, 400–406.
- Kwapinska, M., Horvat, A., Liu, Y., Leahy, J.J., 2019. Pilot Scale Pyrolysis of Activated Sludge Waste from Milk Processing Factory. *Waste Biomass Valorization*, pp. 1–17.
- Langone, M., Basso, D., 2020. Process waters from hydrothermal carbonization of sludge: characteristics and possible valorization pathways. *Int. J. Environ. Res. Publ. Health* 17 (18), 6618.
- Lim, B.H., Kim, D.J., 2017. Selective acidic elution of Ca from sewage sludge ash for phosphorus recovery under pH control. *J. Ind. Eng. Chem.* 46, 62–67.
- Liu, Z., Qian, G., Sun, Y., Xu, R., Zhou, J., Xu, Y., 2010. Speciation evolutions of heavy metals during the sewage sludge incineration in a laboratory scale incinerator. *Energy Fuels* 24 (4), 2470–2478.
- Liu, X., Zhai, Y., Li, S., Wang, B., Wang, T., Liu, Y., Qiu, Z., Li, C., 2020. Hydrothermal carbonization of sewage sludge: effect of feed-water pH on hydrochar's physicochemical properties, organic component and thermal behavior. *J. Hazard Mater.* 388, 122084.
- Lu, T., Yuan, H.R., Zhou, S.G., Huang, H.Y., Noriyuki, K., Chen, Y., 2012. On the pyrolysis of sewage sludge: the influence of pyrolysis temperature on biochar, liquid and gas fractions. In: *Advanced Materials Research*, vol. 518. Trans Tech Publications Ltd, pp. 3412–3420.
- Lucid, J.D., Fenton, O., Healy, M.G., 2013. Estimation of maximum biosolids and meat and bone meal application to a low P index soil and a method to test for nutrient and metal losses. *Water Air Soil Pollut.* 224, 1464.
- Mau, V., Gross, A., 2018. Energy conversion and gas emissions from production and combustion of poultry-litter-derived hydrochar and biochar. *Appl. Energy* 213, 510–519.
- Mau, V., Quance, J., Posmanik, R., Gross, A., 2016. Phases' characteristics of poultry litter hydrothermal carbonization under a range of process parameters. *Bioresour. Technol.* 219, 632–642.
- Milieu, WRC, RPA, 2013a. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report – Part I: Overview Report. Service contract No 070307/2008/517358/ETU/G4.
- Milieu, WRC, RPA, 2013b. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report – Part II: Report on Options and Impacts. Service contract No 070307/2008/517358/ETU/G4.
- Milieu, WRC, RPA, 2013c. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report – Part III: Project Interim Reports. Service contract No 070307/2008/517358/ETU/G4.
- Mollenhorst, H., de Haan, M.H., Oenema, J., Kamphuis, C., 2020. Field and crop specific manure application on a dairy farm based on historical data and machine learning. *Comput. Electron. Agric.* 175, 105599.
- Nanzer, S., Oberson, A., Huthwelker, T., Eggenberger, U., Frossard, E., 2014. The molecular environment of phosphorus in sewage sludge ash: implications for bioavailability. *J. Environ. Qual.* 43 (3), 1050–1060.
- Numviyimana, C., Warchol, J., Izydorczyk, G., Baśladyńska, S., Chojnacka, K., 2020. Struvite production from dairy processing wastewater: optimizing reaction conditions and effects of foreign ions through multi-response experimental models. *J. Taiwan Inst. Chem. Eng.* 117, 182–189.
- O' Donnell, C., Egan, A., Harrington, J., Barnett, D., Forrestral, P., Power, N., 2021. An overview on deficit and requirements of the Irish national soil phosphorus balance. *Sci. Total Environ.* 785, 147251.
- Pankakoski, M., Noicil, 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 effluent treatment plants. *Bull. Int. Dairy Fed.* 356, 4–34.
- Ryan, M.P., Walsh, G., 2016. The Characterisation of Dairy Waste and the Potential of Whey for Industrial Fermentation. EPA Research Report, Environmental Protection Agency, Ireland.
- Teagasc, 2020. In: Wall, D.P., Plunkett, M. (Eds.), Major and micro nutrient advice for productive agricultural crops, fifth ed. Teagasc, Johnstown Castle, Wexford, Ireland.
- Tian, F., Li, B., Chen, Y., Li, C., 2002. Formation of NOx precursors during the pyrolysis of coal and biomass. Part V. Pyrolysis of a sewage sludge. *Fuel* 81 (17), 2203–2208.
- Timoney, Fehily, Company, 1999. Codes of Good Practice for the Use of Biosolids in Agriculture. Guidelines for Farmers. Environ. <http://www.environ>.

- ie/en/Publications/Environment/Water/FileDownload,17228,en.pdf. (Accessed 19 June 2012).
- Wang, T., Zhai, Y., Zhu, Y., Peng, C., Wang, T., Xu, B., Li, T., Zeng, G., 2017. Feedwater pH affects phosphorus transformation during hydrothermal carbonization of sewage sludge. *Bioresour. Technol.* 245, 182–187.
- Wei, L., Wen, L., Yang, T., Zhang, N., 2015. Nitrogen transformation during sewage sludge pyrolysis. *Energy Fuels* 29 (8), 5088–5094.
- Western Australia, 2012. Department of Environment and Conservation. Environmental Regulation Division, Author. Department of Environment and Conservation, Perth, WA. Western Australian guidelines for biosolids management.
- Yetilmezsoy, K., Ilhan, F., Kocak, E., Akbin, H.M., 2017. Feasibility of struvite recovery process for fertilizer industry: a study of financial and economic analysis. *J. Clean. Prod.* 152, 88–102.
- Yuan, J., Xu, R., Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour. Technol.* 102, 3488–3497.
- Yuan, H., Lu, T., Wang, Y., Chen, Y., Lei, T., 2016. Sewage sludge biochar: nutrient composition and its effect on the leaching of soil nutrients. *Geoderma* 267, 17–23.
- Zhang, J., Zuo, W., Tian, Y., Chen, L., Yin, L., Zhang, J., 2017. Sulphur transformation during microwave and conventional pyrolysis of sewage sludge. *Environ. Sci. Technol.* 51 (1), 709–717.