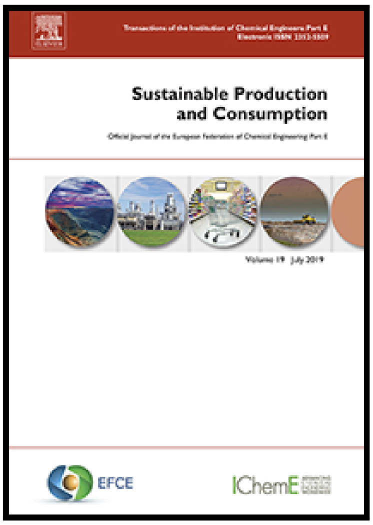

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Grassland Phosphorus and Nitrogen Fertiliser Replacement value of Dairy Processing Dewatered Sludge

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Abstract

Dairy processing sludge is currently a bio-based fertiliser being spread to grassland without knowledge pertaining to its phosphorus (P) or nitrogen (N) fertiliser replacement value. This creates uncertainty of desired crop yield achievement and unproductive nutrient recycling and also poses a great challenge to the dairy milk processing industry in promoting their food processing by-product as valuable recyclable fertiliser. Therefore four representative samples, i.e. two activated sludge (aluminium-precipitated (Al-sludge) and iron-precipitated (Fe-sludge)), and two lime-stabilised calcium-precipitated sludge (Ca_1- and Ca_2-sludge), were examined at field scale to assess P and N availability for crop yield and uptake in comparison to reference mineral fertilisers over one seasonal year. The field plots were set-up on a light textured clay loam soil within the optimum plant available P (Morgan's soil P index 3, i.e. medium / adequate soil P level) in two separate adjoining areas consisting of P and N availability experiments. Each experiment consisted of 40 plots (each 8×2 m^2) of 10 treatments with 4 replications arranged in a randomised complete block design. All dairy sludge (40 kg-P ha^{-1}) and mineral P treatments (rates 0–50 kg-P ha^{-1}) produced similar yields and uptake, and crop P was not affected by sludge applications despite the presence of high Al, Ca and Fe. During the experiment there was no significant change in P index (stayed at index 3) indicating that no treatment caused a decline in P into index 2 (i.e. low soil P level), therefore replacing P removed by the crop. The only change in Morgan's P was observed in the Ca-sludge treatments, but this was due to Morgan's reagent overestimating plant available P in high Ca conditions. From N trial plots a significantly higher grass yield and N uptake was observed for Fe and both Ca-type sludge applied plots than the control (zero N) plot during the 1st harvest, while no statistical difference observed in the subsequent harvests (up to 4th harvesting). The N fertiliser replacement value (derived from mineral N response) of sludge samples was observed to be in the order of Fe (54%) > Ca2 (25%) > Ca1 (22%) > Al (8%) with greater promise of N fertiliser efficiency of Fe and Ca types. Overall these bio-based sludges show promise in recycling P and N for grassland application but longer term trials in other soil types considering other environmental aspects (losses to soil, water and air) can further optimize the management of dairy sludge as an alternative to chemical fertiliser.

Keywords

Dairy food processing sludge, nitrogen and phosphorus recycling, crop yield, fertiliser replacement value, grassland application.

Abbreviations

Al-DPS	aluminium rich activated sludge
Ca-DPS	calcium-phosphorus rich lime treated sludge
CAN	calcium ammonium nitrate
DM	dry matter
DPS	dairy processing sludge
Fe-DPS	iron rich activated sludge
FRV	fertiliser replacement value
FW	fresh weight
OM	organic matter

P_m	Morgan's soil phosphorus concentration
TC	total carbon
TSP	triple super phosphate.

1. Introduction

The new European Union (EU) Fertilising Products Regulation (EU, 2019) has expanded its scope to enable the use of recovered and bio-based fertilising products in line with EU Circular Economy Package goals adopted in December 2015 (EC, 2015). Such an initiative to increase the use of organic and waste-based recycling-fertiliser products for agronomic benefit can help to embrace the sustainability within the agro-industrial food supply chain. The dairy industry in Europe is one of the largest agri-food sectors, which generates huge volumes of food processing wastewater treated sludge (Erkan et al., 2018). For example, dairy processing sludge (DPS) from the dairy industry is a growing bio-based residue in Ireland with a 39% increase observed between the period 2012−2017, which came to 126,718 tonnes (wet weight) in 2017 (Ashekuzzaman et al., 2019). Recent figures show that in Ireland, 63% of the DPS is land spread, 13.6% is used for composting and the remaining is removed by licensed contractors which ultimately land spread after treatment from anaerobic digestion, drying, and vermicomposting (Ryan and Walsh, 2016; Foster, 2006). Although, land application of DPS is seen within the dairy processing industry as a short to medium term solution as a disposal option, it may continue in many countries such as Ireland for a long time to come. Presently two major knowledge gaps exist - a) the crop available fraction of phosphorus (P) and nitrogen (N), and b) the P and N fertiliser replacement value (FRV) of the major DPS types.

The crop available fraction of N and P varies widely across different bio-based wastes. For example, N FRV was reported to be for spent yeast waste 89%, liquid thermophilic aerobic digestate of food waste 59–76%, anaerobic co-digestate of livestock slurries and food waste 68–85%, dewatered mesophilic anaerobically digested biosolids 50–52%, dewatered mesophilic anaerobically digested organic fraction of municipal solid waste 52%, vegetable processing waste 45%, and salty whey 41% (Rigby and Smith, 2014). For P-FRV, the values reported were 55–86% for ashes (from oat grain, wheat straw), 64–67% for biogas residue (from crop, slaughterhouse waste), 64% for chicken manure, 65% for brewer's spent grain, 59% for cattle slurry, 60% for meat meal, 44% for bone meal, and 13–63% for sewage sludge (lowest for Ca-precipitated and highest for Fe-precipitated) (Delin, 2016). Such uncertain fertiliser efficiency is one of the major challenges of using organic wastes in agroecosystems for soil nutrient cycling (Bernal, 2017). To the best of our knowledge, there is no known equivalent FRV data source for DPS. Research on the potential valorisation of DPS is relatively a new area with limited recent publications available looking into energy recovery (Kwapinska et al., 2020), hydrothermal carbonization (Atallah et al., 2020) and DPS derived carbonaceous adsorbent for P removal from water (Ashekuzzaman et al., 2020a) as an alternative to direct land application. A temporal nutrient database developed by Ashekuzzaman et al. (2019) showed DPS samples are significantly higher in N and P when compared to cattle slurry and farmyard manure. Only a limited number of past studies investigated DPS for forage production which indicated its promise as fertiliser in supplying nutrients and improving soil fertility (Lopez-Mosquera et al., 2002; Brown et al., 1990).

Growers need to know the N and P FRV of DPS in order to effectively incorporate DPS into fertiliser programmes. Previously, grassland research has made it possible to successfully incorporate waste products such as cattle slurry and biosolids into fertiliser programmes as organic fertilisers with a known FRV (Sullivan et al., 2015; Lalor et al., 2010). In Ireland, cattle slurry is commonly used as an organic fertiliser for grassland application with a typical value of 1,000 gallons of cattle slurry applied by broadcast in springtime having an available N-P-potassium (K) content equivalent to a 50 kg bag of 6-5-30 mineral fertiliser (Plunkett and Wall, 2016). In terms of FRV for biosolids field data showed that the first year plant-available N and P were 35 and 40%, respectively (Sullivan et al., 2015).

The DPS sample composition is presented in Table 1. The concentrations of aluminium (Al), iron (Fe) and calcium (Ca) are typically associated with the addition of Al, Fe salts, and lime during wastewater treatment to remove P from the secondary effluent. The composition analysis of 63 DPS samples from nine dairy food processing wastewater treatment sites showed that Al, Fe, Ca and P content varies greatly as there is no standard chemical treatment use across different processing sites (Ashekuzzaman et al., 2019). Previous research found a link between the amount of Al and Fe in wastewater treated sludge with P availability to plants. This is particularly relevant to sewage wastewater treated biosolids which depending on the total concentration of Al and Fe content, have from 27 to 85% P bioavailability (Khiari et al., 2020). The amount of Ca content exceeding a molar Ca:P ratio of 2 in organic fertilisers (e.g. compost and biochar) also can negatively affect the P availability for plant uptake due to formation of low soluble Ca-P compounds such as hydroxyl-apatite ($Ca_3(PO_4)_2Ca(OH)_2$) (Vanden Nest et al., 2021). Hence DPS samples which are high in Ca, Al and Fe were chosen in this study for their agronomic nutrient recycling assessment. The objective of the present study was to examine these DPS products in terms of their nutrient availability to grass and their respective P and N FRV. For that purpose the major DPS types were collected, characterised and applied to a field designed experiment. Results for grass dry matter yield, herbage mineral concentration and plant available soil P levels were investigated over a 12 month period.

2. Materials and methods

2.1 Dairy processing sludge (DPS)

Four DPS samples – 1) activated sludge aluminium-precipitated ("Al-DPS"), 2) activated sludge iron-precipitated ("Fe-DPS"), 3) lime-stabilised sludge calcium-precipitated ("Ca_1-DPS"), and 4) lime-stabilised sludge Ca-precipitated ("Ca_2-DPS") were tested in this study that represents the main DPS type applied to grassland in Ireland. The activated sludge is generated after dairy food processing wastewater treatment using aeration and a biological floc formation including the dosing of alum or ferric salt (aluminium or iron flocculent) to remove P. Due to this common process, Al-DPS and Fe-DPS are the dominant sludge types generated by dairy companies. On the other hand, Ca_1-DPS and Ca_2-DPS are generated after dissolved air floatation (DAF) technique of treating dairy wastewater rich in fats, oils and greases, and these sludges are high in Ca-P. The physicochemical properties of the DPS samples are presented in Table 1 whereby the DPS composition reflects the processing stream it originates from. The details on the DPS characterisation profile and method can be found in the recent paper by Ashekuzzaman et al. (2019). 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 a 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.

Table 1 Physicochemical characteristics of DPS.

Sample	DM	OM	TC	pH	N	NH_4-N	P	K	S	Ca	Al	Fe
	% FW	% DM	% DM					g Kg^{-1} DM				
Ca_1-DPS	22	44.5	22.5	6.7	36.5	1.0	79.6	3.9	2.9	238	0.6	0.5
Ca_2-DPS	31	19.8	9.6	7.7	19.3	0.5	128	4.0	3.2	278	0.9	3.8
Fe-DPS	20	47.0	22.3	7.4	38.5	1.9	31.6	5.5	3.3	107	0.8	162
Al-DPS	11	61.7	25.3	7.2	42.5	2.5	34.1	5.7	4.3	33	58	4.1

DPS: dairy processing sludge; Ca_1 and Ca_2-DPS: calcium-phosphorus rich lime treated sludge; Al-DPS: aluminium rich activated sludge; Fe-DPS: iron rich activated sludge; FW: fresh weight; DM: dry matter; OM: organic matter; TC: total carbon

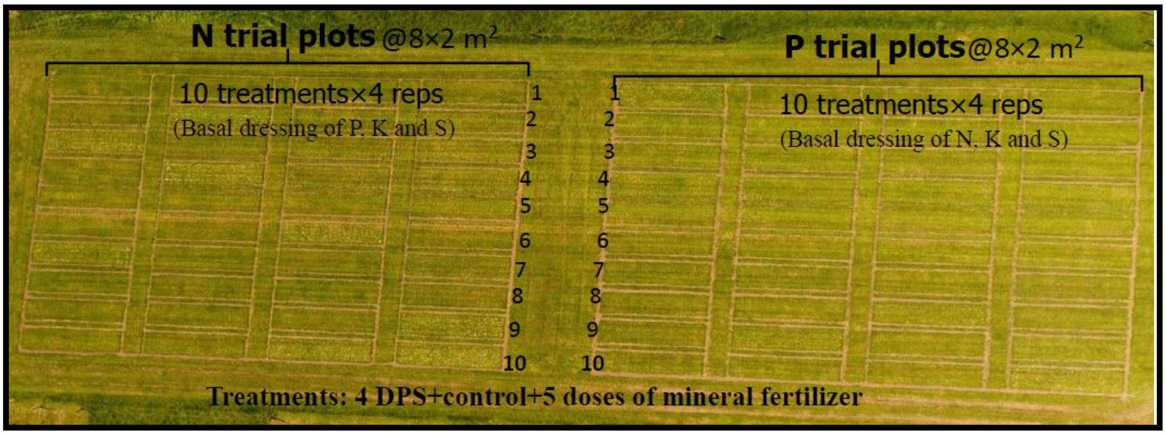
2.2 Field plots and experimental set-up

This investigation was conducted in temperate grassland (on a grass sward dominated by perennial ryegrass) at Teagasc, Johnstown Castle Research Farms, Co. Wexford (latitude 52˚ 17′N, longitude 6˚ 29′W) in the southeast of Ireland (please see supplementary Figure S1 for photographic sequence of experimental site layout, application of treatments and harvesting). The experimental site was light textured clay loam with a 0−10 cm Morgan’s soil test P level of 6.8 mg L^{-1} and a Mehlich-3 soil test P of 52.9 mg kg^{-1}. The Morgan’s test is used in Ireland as the basis for agronomic recommendations and legal P application rate determination (Teagasc, 2016; Brennan et al., 2011), while the Mehlich-3 soil P test is more widely used internationally and is presented for comparison. Based on the Morgan's reagent extractable P concentration, P index system (as outlined in Table S3) has been developed in Ireland to show the plant available soil P concentration level. The average soil properties of the surface 10 cm soil layer prior to the application of treatments were pH 6.6, total carbon 3.8%, total organic carbon 2.8%, total N 0.4%, and Morgan’s extractable potassium (K) 103.6 mg L^{-1}, magnesium (Mg) 129.5 mg L^{-1}.

The field plots were set-up in two separate adjoining experiments consisting of N and P trial plots (Figure 1). The experiment designed for each was a randomised complete block. Each experiment consisted of 40 plots (each 8×2 m^2) consisting of 4 blocks within which the 10 experimental treatments were randomly assigned. The experimental treatments for the N trial were five rates of calcium ammonium nitrate (CAN) mineral fertilizer treatments of 20, 40, 60, 80 and 100 kg N ha^{-1}, four DPS treatments at 60 kg N ha^{-1}, and one treatment with no N (control). Basal dressing of P (44 kg ha^{-1}), K (100 kg ha^{-1}) and S (20 kg ha^{-1}) were applied to all plots at the beginning of the experiment and also after each harvest with same rates of K and S but for P at 15 kg ha^{-1} across all treatments to ensure that N was the only limiting nutrient in the N FRV experiment.

In the P FRV experiment triple super phosphate (TSP) mineral fertiliser was applied at rates 10, 20, 30, 40 and 50 kg P ha^{-1}, DPS was applied at 40 kg P ha^{-1} and one treatment with no P (control). A basal dressing of N (130 kg ha^{-1}), K (100 kg ha^{-1}) and S (20 kg ha^{-1}) was applied at the beginning and also after each harvest with same rates to ensure that only P was yield-limiting nutrient. This experiment was limited to one seasonal year with single application of mineral and DPS fertilisers and occurred on a single soil type.

The buffer distance between plots alongside each other was 0.5 m and in between replicates 2 m. The treatments (including DPS and different rates of N and P mineral fertilisers) were applied to the plots by hand spreading following a distribution as even as possible to cover each plot area. In order to get an even application treatments were applied walking up and down the plots a minimum of three times. The basal dressing with mineral fertilisers was applied using a barrow applicator which covers a two meter width.



Block 1	Block 2	Block 3	Block 4
1	1	5	8
2	2	7	1
3	7	3	10
4	5	6	2
5	6	8	9
6	9	10	5
7	4	2	7
8	10	4	3
9	3	1	4
10	8	9	6

Randomly assigned N treatments

Block 1	Block 2	Block 3	Block 4
1	9	8	9
2	3	1	8
3	1	2	3
4	7	4	6
5	10	5	5
6	6	10	10
7	8	6	7
8	4	9	2
9	2	7	4
10	5	3	1

Randomly assigned P treatments

Figure 1 Aerial view of 80 grassland plots with the layout of randomly assigned treatments used in this study.

2.3 Harvests, crop and soil analysis

Four harvests were conducted between June to October 2017 (07/06/17, 18/07/17, 14/09/17 and 18/10/17) in both N and P trial plots after a single application of all treatments in 24th April 2017. For P trial plots, two more harvests were taken in the following year (22/03/18 and 29/05/2018) to assess any residual effect of P on crop yield. Basal dressings were applied on 24/04/17, 09/06/17, 21/07/17 and 18/09/17, respectively. An additional basal dressing was applied in P trial plots on 26/03/18. Plots were harvested using a Haldrup (Deutz Fahr) grass harvester which has a cut width of 1.5 m and cut at a height of 5 cm (Figure S1 in supplementary material). Plots were harvested taking cuttings from the centre. Fresh weights of the harvested grass from each plot were measured and then sub-sampled for dry matter (DM) and chemical analysis.

In the laboratory, fresh subsamples of grass were weighed and then dried in perforated plastic bags in an oven at 70˚C for 72 hours. Once dried dry weight was recorded for DM analysis and subsequently, dried samples were grounded and 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 (representative composite sample for each plot) of top 10 cm below the ground surface were collected pre and post application of treatments and were placed in a small cardboard box labelled with the plot number. In order to achieve a representative sample from each plot, the plots were sampled lengthways from front to back in a “W” shaped pattern. In order to achieve this, a minimum of 6 samples were taken from each plot. Samples were then dried in the oven at 40˚C for 72 hours and subsequently ground using a mechanical 2 mm soil sieving machine in preparation for chemical analysis. Both Mehlich-3 and Morgan extractable P were analysed to assess the effect of treatments on soil P pools. These are agronomic soil P testing methods that quantify the plant available and labile P fractions (Daly and Casey, 2003). Morgan's extracting (Morgan, 1941) solution was used to determine extractable P, K, Mg and LR, and Mehlich-3 (M3) extracting solution (Mehlich, 1984) was used to determine extractable M3-P, M3-K, M3-Mg, M3-Al, M3-Fe and M3-Ca. Morgan’s solution was prepared by combining 740 ml of 40% sodium hydroxide and 720 ml of glacial acetic acid and making a final volume about 10 L with the addition of distilled water. The solution pH was adjusted to 4.8. Soil samples were mixed with the Morgan's solution in a 1:5 (v/v) soil to solution ratio and shaken for 30 min. The solutions were then filtered and analysed on the Lachat system (Lachat QuickChem 8500 Series 2 continuous flow analyser) colorimetrically for P and Mg, and photometrically for K. Mehlich-3 solution was prepared from 0.2M Acetic acid (CH_3COOH), 0.25M Ammonium nitrate (NH_4NO_3), 0.015M Ammonium fluoride (NH_4F), 0.013M Nitric acid (HNO_3) and 0.001M Ethylenediaminetetraacetic acid (EDTA) and has a pH of about 2.5. Soil samples were mixed with the Mehlich-3 solution (2 g in 20 ml solution), shaken for 5 min, then filtered and analysed using ICP-OES for total concentrations of desired elements. Due to reagent differences, the Morgan test and the Mehlich-3 test measure different fractions of the total amount of P in the soil where Mehlich-3 solution can extract about 3 to 30 times more P than Morgan's extract depending on soil types, pH, textural class, and content of Al, Fe and Ca (Ketterings and Czymmek, 2002). For example, fluoride and nitric acid present in the Mehlich-3 solution mainly aid extraction of Fe, Al and Ca phosphate anions and metal cations. On the other hand, Morgan's solution is designed to dissolve plant available P i.e. orthophosphate ion (PO_4^{3-}) in soil extracts which was analysed colorimetrically. Soil pH was determined using a pH probe (Jenway 3510 pH meter) and a 2.5:1 ratio of deionized water-to-soil. Total carbon (TC) and total N were measured by high temperature combustion method.

2.4 Data analysis and statistics

Mineral fertiliser N and P treatments at different application rate were used to calculate the mineral fertiliser N and P response curves for the site. The experimental site was non-responsive to mineral P application rate, hence a P response curve could not be generated to calculate P FRV of tested sludge samples. The N uptake in the DPS treatments were compared against the respective mineral N fertiliser response in order to calculate the FRV (expressed as a percentage of total N applied in DPS) as per eq. (1). This means the N FRV of different DPS provides an estimation of the percentage of total N in the applied DPS that is equivalent to the amount of mineral fertilizer required to attain the same N uptake level (Delin, 2011).

$$\text{N FRV (\%)} = \frac{EQ_{mineral\ N\ fertiliser\ rate}}{N_{applied}} \times 100 \qquad (1)$$

where N FRV (%) is the percentage of mineral N fertiliser equivalence of DPS, $EQ_{\text{mineral N fertiliser rate}}$ is the equivalent of amount of mineral N fertiliser that returns the same response (e.g. N uptake) compared to DPS, and N_{applied} is the amount of DPS P applied. The equivalent mineral fertiliser ($EQ_{\text{fertiliser}}$) is determined using the regression between mineral fertiliser application rates (kg ha^{-1}) and crop response (N uptake or yield). In this study the best fit of mineral N fertiliser application rates and their corresponding N uptake provided a linear regression.

When mineral fertiliser application of multiple rates is not included in the experimental design, then N-FRV of a residue treatment can be calculated using the ratio of apparent N recovery (eq. 3) for the treatment to that of a reference mineral fertiliser as per below eq. (2) (Sigurnjak et al., 2019). In this study, DPS treatments were applied at 60 kg-N ha^{-1} in N trial plots, so mineral N fertiliser applied at this rate can be considered as a reference and no N treatment as a control. The N replacement use efficiency (N-RUE) of DPS treatments with respect to a mineral fertiliser equivalent was also calculated as per eq. (4) (Sigurnjak et al., 2019).

N fertiliser replacement value (N FRV in %)

$$= \frac{\frac{N\ uptake\ DPS - N\ uptake\ control}{total\ N\ applied\ DPS}}{\frac{N\ uptake\ Reference - N\ uptake\ control}{total\ N\ applied\ Reference}} \times 100 \qquad (2)$$

Apparent N recovery

$$= \frac{N\ uptake\ DPS - N\ uptake\ for\ the\ control}{Total\ N\ applied\ DPS} \times 100 \qquad (3)$$

N replacement use efficiency (N-RUE in %)

$$= \frac{\frac{N\ uptake\ DPS}{total\ N\ applied\ DPS}}{\frac{N\ uptake\ Reference}{total\ N\ applied\ Reference}} \times 100 \qquad (4)$$

Statistical analysis was performed using SAS statistical software (SAS, Statistical Analysis System, 2013). The PROC GLIMMIXED procedure of SAS was used to determine the effect of the fertiliser treatments on the response variables of crop yield, crop P and N concentration and uptake.

3. Results and discussion

3.1 P availability and P-FRV

In P experiment, the cumulative grass DM yield and P uptake were not statistically different across four DPS treatments and these were similar to those observed for the zero P treatment (Table 2, Table 3). The cumulative uptake pattern of P for TSP fertiliser applied plots was also similar except for the highest application rate of 50 kg ha^{-1}. The TSP-50 applied pots showed significantly higher P uptake compared to the zero P and plots receiving DPS (Table 3). The grass P uptake and P concentrations across six harvests did not show any particular trend although having differences in P treatments, and these were overall similar to those observed in no P treatment (Table 3, Table 4). In general, the grass growth and P uptake pattern were not statistically different between the experimental treatments.

The experimental site had Morgan's soil test P of 6.8 mg L^{-1} (P Index 3, i.e. medium or adequate plant available soil P level). The field data of yield and P uptake indicated that the site was non-responsive to mineral P application rate between 0−40 kg ha^{-1}. As there was minimal response to P at the site, the P-FRV of the applied DPS treatments could not be derived. However, there was no significant difference in performance of DPS products compared to the TSP mineral fertiliser applied at P Index 3. This is a significant finding in of itself because the DPS products were high in Ca, Fe and Al, which was associated with dairy processors chemical use for treating wastewater (Table 1, Table 5). These elements are known to fix plant available P into unavailable forms in Irish soils (Daly et al., 2015; Wendling et al., 2013) thus prior to this study a negative effect could not be ruled out. No evidence observed for any significant increase of soil elemental concentrations of Ca, Al and Fe in DPS applied plots (supplementary Figure S2). However, the long-term impacts of these metals to crop and soil microbiology is an important aspect to investigate. With respect to the EU regulated heavy metals, the ingestion of heavy metals to soil from dairy sludge land spreading is very low when compared to the limit of average annual rate of addition of metal such as Cr: 3.5, Cu: 7.5, Ni: 3.0, Pb: 4.0 and Zn: 7.5 kg ha^{-1} $year^{-1}$ over a 10-year period as recommended in the "Codes of Good Practice for the Use of Biosolids in Agriculture" (Fehily Timoney Company, 1999; Lucid et al., 2013). Also, such metal concentrations are not likely to be harmful for grassland pasture comparing the values of phytotoxic concentrations in ryegrass (Ashekuzzaman et al., 2019). In another relevant study using dairy processing sludge (as nutrient source) for grassland fertilisation over a period of 4 years, Lopez-

Mosquera et al. (2000) observed that heavy metal contents (Hg, Pb, Cd, Cu, Zn, Ni and Cr) in both soil and grass tissue did not exceed the EU legislative limits. In terms of impact due to Al or Fe on crop and soil microbiology no adverse effect yet reported for dairy processing sludge. In this aspect, the reference could be used from long-term sewage sludge application to agricultural land as sewage sludge also has high concentration of Fe or Al depending on the chemical precipitant (e.g. alum or ferric chloride) used for P removal process during wastewater treatment process (Khiari et al., 2020). According to Khiari et al. (2020) P uptake by crop from sewage sludge derived biosolids can be affected by their total [Al+Fe] content with predictions of very high, high, medium and low P bioavailability corresponding to the [Al+Fe] total concentration of [260–400], [400–1100], [1100–2800] and [2800–4600] mmol kg^{-1}, respectively. A number of studies reported that repeated application of sewage sludge for long-term (e.g. 10–30 years) increase the concentrations of some heavy metals (mainly Cu and Zn) in soils, however the amounts of metals added to soil with sewage sludge were neither found to be toxic for microbes nor increased uptake of heavy metals in crop (Börjesson et al., 2014; Borjesson and Katterer, 2018; Nicholson et al., 2018). In comparison to sewage sludge, dairy processing sludge contains much lower quantities of heavy metals as observed from two year seasonal composition analysis of 63 samples from six major dairy companies in Ireland (Ashekuzzaman et al., 2019).

Table 2 Effect of treatment and rate on the grass dry matter yield over the course of the P-FRV experiment. Harvesting dates were 07/06/17, 18/07/17, 14/09/17, 18/10/17, 22/03/18 and 29/05/18. Values indicated in brackets are standard deviations (n=4).

Treatment	P rate	Harvest						
		1	2	3	4	5	6	Cumulative
	kg ha^{-1}	Yield (kg DM ha^{-1})						

No P	0	5618 ^{ab}	2736 ^{a}	3562 ^{ac}	291 ^{a}	877 ^{a}	7526 ^{a}	20610 ^{ab}
		(750)	(410)	(158)	(47)	(144)	(749)	(1162)
TSP	10	5544 ^{ab}	2991 ^{a}	3906 ^{abc}	288 ^{a}	1059 ^{a}	7515 ^{a}	21302 ^{a}
		(263)	(490)	(265)	(102)	(362)	(607)	(1513)
TSP	20	5383 ^{ab}	2925 ^{a}	3696 ^{abc}	282 ^{a}	997 ^{a}	7387 ^{a}	20670 ^{ab}
		(288)	(466)	(533)	(80)	(89)	(600)	(791)
TSP	30	4700 ^{cd}	2820 ^{a}	4082 ^{ab}	304 ^{a}	806 ^{a}	7437 ^{a}	20148 ^{abc}
		(522)	(482)	(744)	(52)	(310)	(163)	(1652)
TSP	40	5100 ^{bc}	2820 ^{a}	3618 ^{abc}	262 ^{a}	564 ^{a}	7178 ^{a}	19541 ^{bc}
		(596)	(933)	(343)	(40)	(246)	(786)	(2103)
TSP	50	5817 ^{a}	2778 ^{a}	3603 ^{ac}	297 ^{a}	909 ^{a}	7444 ^{a}	20847 ^{ab}
		(1074)	(523)	(339)	(71)	(270)	(637)	(1657)
Ca_1-DPS	40	5089 ^{bc}	2492 ^{a}	3344 ^{c}	274 ^{a}	725 ^{a}	7036 ^{a}	18961 ^{c}
		(852)	(285)	(330)	(66)	(347)	(615)	(1630)
Ca_2-DPS	40	5304 ^{abc}	2413 ^{a}	4254 ^{b}	297 ^{a}	951 ^{a}	6916 ^{a}	20136 ^{abc}
		(301)	(560)	(574)	(77)	(168)	(317)	(958)
Al-DPS	40	5028 ^{c}	2927 ^{a}	3687 ^{abc}	310 ^{a}	1122 ^{a}	7158 ^{a}	20232 ^{abc}
		(1246)	(305)	(519)	(36)	(202)	(632)	(974)
Fe-DPS	40	5277 ^{abc}	2490 ^{a}	3706 ^{abc}	234 ^{a}	972 ^{a}	7327 ^{a}	20005 ^{bc}
		(575)	(221)	(399	(27)	(167)	(319)	(542)

Mean comparison by *F*-protected LSD test ($P \leq 0.05$); Within columns shared letters denote no difference ($p > 0.05$), and unshared letters denote a statistical difference ($p < 0.05$); DPS: dairy processing sludge; Ca_1 and Ca_2-DPS: calcium-phosphorus rich lime treated sludge; Al-DPS: aluminium rich activated sludge; Fe-DPS: iron rich activated sludge; TSP: triple super phosphate.

Table 3 Effect of treatment and rate on grass P uptake across 6 consecutive harvestings* between June 2017 − May 2018. Values indicated in brackets are standard deviations (n=4).

Treatment	P rate	Harvest						
		1	2	3	4	5	6	Cumulative
	kg ha^{-1}	P uptake (kg-P ha^{-1})						
No P	0	16.5^{bcd}	7.5^{a}	11.3^{c}	1.0^{a}	2.8^{a}	16.9^{ab}	56.0^{bcd}
		(1.3)	(1.3)	(0.5)	(0.0)	(0.7)	(3.1)	(5.4)
TSP	10	18.3^{ab}	8.3^{a}	13.3^{abc}	1.3^{a}	3.6^{a}	16.8^{ab}	61.6^{ab}
		(1.5)	(1.5)	(1.0)	(0.5)	(1.5)	(2.1)	(4.7)
TSP	20	18.8^{ab}	8.5^{a}	13.0^{abc}	1.3^{a}	3.5^{a}	15.7^{abc}	60.8^{abc}
		(1.7)	(2.5)	(3.6)	(0.5)	(0.5)	(1.4)	(3.3)
TSP	30	16.0^{cd}	8.0^{a}	14.0^{ab}	1.0^{a}	2.6^{a}	15.2^{abc}	56.8^{bcd}
		(2.4)	(1.6)	(2.8)	(0.0)	(1.0)	(2.4)	(8.2)
TSP	40	18.0^{abc}	7.8^{a}	13.3^{abc}	1.0^{a}	1.9^{a}	14.1^{c}	56.1^{bcd}
		(2.2)	(2.8)	(1.5)	(0.0)	(0.7)	(2.1)	(4.1)
TSP	50	19.8^{a}	8.5^{a}	13.3^{abc}	1.3^{a}	3.3^{a}	17.3^{a}	63.5^{a}
		(2.6)	(1.9)	(1.5)	(0.5)	(1.1)	(2.1)	(5.5)
Ca$_1$-DPS	40	14.8^{d}	6.8^{a}	11.3^{c}	1.3^{a}	2.8^{a}	17.1^{a}	54.1^{cd}
		(3.0)	(1.0)	(1.0)	(0.5)	(1.4)	(1.6)	(5.0)
Ca$_2$-DPS	40	14.8^{d}	6.3^{a}	14.3^{a}	1.0^{a}	3.3^{a}	14.9^{bc}	54.6^{d}
		(0.5)	(2.2)	(1.5)	(0.0)	(0.6)	(1.0)	(3.1)
Al-DPS	40	14.8^{d}	8.5^{a}	11.5^{c}	1.0^{a}	3.5^{a}	16.0^{abc}	55.3^{bcd}
		(3.3)	(1.3	(1.7)	(0.0)	(0.8)	(2.0)	(4.8)
Fe-DPS	40	14.8^{d}	6.3^{a}	11.8^{bc}	1.0^{a}	3.4^{a}	16.6^{ab}	53.9^{d}
		(1.5)	(1.3)	(1.7)	(0.0)	(0.9)	(2.6)	(2.6)

Mean comparison by *F*-protected LSD test ($P \leq 0.05$); Within columns shared letters denote no difference ($p > 0.05$), and unshared letters denote a statistical difference ($p \leq 0.05$); * Harvesting on 07/06/17, 18/07/17, 14/09/17, 18/10/17, 22/03/18 and 29/05/18.

Table 4 Effect of treatment and rate on grass P concentrations across 6 consecutive harvestings* between June 2017 − May 2018. Values indicated in brackets are standard deviations (n=4).

Treatment	P rate	Harvest					
		1	2	3	4	5	6
	kg ha^{-1}	P concentration (% of DM)					
No P	0	0.30^{bc}	0.27^{bcd}	0.32^{b}	0.39^{bc}	0.32^{c}	0.23^{ab}
		(0.02)	(0.03)	(0.02)	(0.04)	(0.06)	(0.02)
TSP	10	0.33^{ab}	0.29^{ab}	0.33^{ab}	0.40^{abc}	0.34^{bc}	0.23^{ab}
		(0.03)	(0.02)	(0.02)	(0.02)	(0.03)	(0.02)
TSP	20	0.35^{a}	0.30^{ab}	0.35^{ab}	0.44^{a}	0.35^{abc}	0.21^{ab}
		(0.03)	(0.04)	(0.06)	(0.03)	(0.02)	(0.01)
TSP	30	0.34^{a}	0.28^{bcd}	0.34^{ab}	0.41^{abc}	0.33^{c}	0.20^{b}
		(0.04)	(0.03)	(0.03)	(0.03)	(0.02)	(0.03)
TSP	40	0.35^{a}	0.27^{cd}	0.37^{a}	0.42^{ab}	0.34^{bc}	0.20^{b}
		(0.01)	(0.01)	(0.02)	(0.05)	(0.03)	(0.04)
TSP	50	0.34^{a}	0.31^{a}	0.37^{a}	0.44^{a}	0.36^{ab}	0.23^{ab}
		(0.03)	(0.02)	(0.01)	(0.04)	(0.03)	(0.01)
Ca_1-DPS	40	0.29^{bc}	0.26^{cd}	0.34^{ab}	0.44^{a}	0.38^{a}	0.25^{a}
		(0.02)	(0.01)	(0.02)	(0.02)	(0.02)	(0.03)
Ca_2-DPS	40	0.29^{c}	0.26^{c}	0.33^{ab}	0.40^{abc}	0.35^{abc}	0.22^{ab}
		(0.02)	(0.02)	(0.02)	(0.03)	(0.02)	(0.02)
Al-DPS	40	0.30^{bc}	0.29^{ab}	0.31^{b}	0.38^{c}	0.32^{c}	0.23^{ab}
		(0.01)	(0.03)	(0.03)	(0.02)	(0.02)	(0.03)
Fe-DPS	40	0.28^{c}	0.25^{c}	0.32^{b}	0.39^{bc}	0.35^{abc}	0.23^{ab}
		(0.02)	(0.03)	(0.02)	(0.03)	(0.04)	(0.04)

Mean comparison by *F*-protected LSD test ($P \leq 0.05$); Within columns shared letters denote no difference ($p > 0.05$), and unshared letters denote a statistical difference ($p \leq 0.05$); * Harvesting on 07/06/17, 18/07/17, 14/09/17, 18/10/17, 22/03/18 and 29/05/18.

Table 5 DPS associated Ca, Al, Fe, TC and OM input to soil.

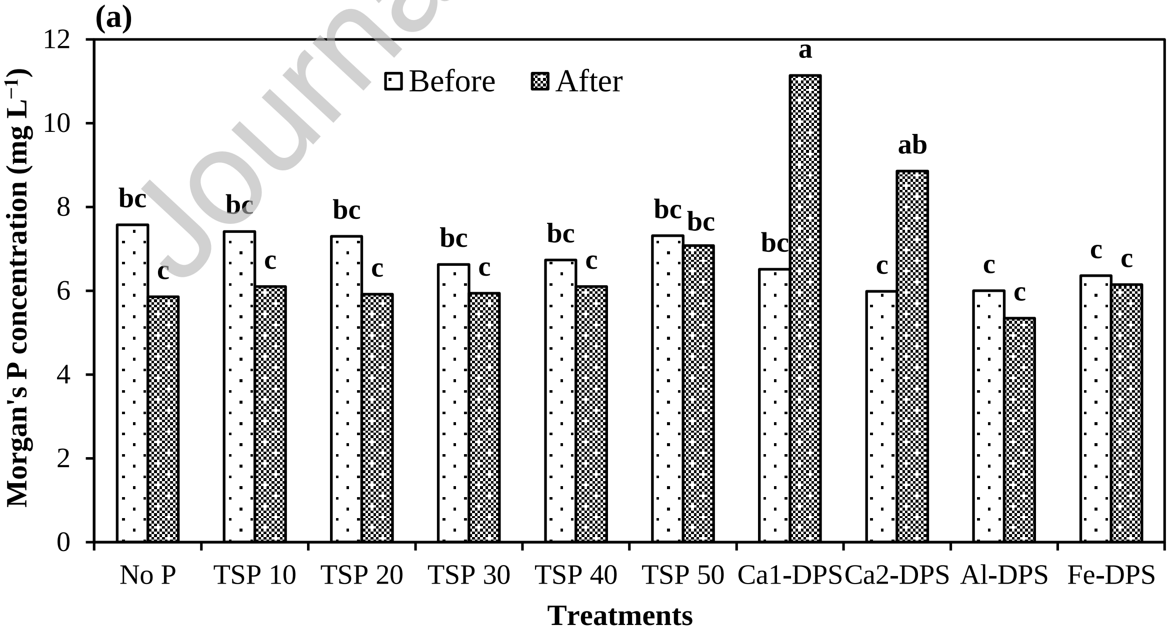
Treatment	P	FW	Ca	Al	Fe	TC	OM
	kg ha^{-1}	tonne ha^{-1}	kg ha^{-1}	kg ha^{-1}	kg ha^{-1}	kg ha^{-1}	kg ha^{-1}
Ca$_1$-DPS	40	2.3	118	0.3	0.2	111	220
Ca$_2$-DPS	40	1.0	86	0.3	1.2	30	61
Fe-DPS	40	6.3	135	1.0	204	282	593
Al-DPS	40	10.6	39	67.8	4.8	296	721

DPS: dairy processing sludge; Ca$_1$ and Ca$_2$-DPS: calcium-phosphorus rich lime treated sludge; Al-DPS: aluminium rich activated sludge; Fe-DPS: iron rich activated sludge; FW: fresh weight; OM: organic matter; TC: total carbon

3.2 Soil P change at the end of the experiment

There was no significant difference in agronomically available Morgan or Mehlich-3 extractable P values in pre- and post-harvest (Figure 2) and soil in most plots remained within Morgan's soil P Index 3 despite removal of between 53.9 and 61.5 kg-P ha^{-1} over the course of the experiment (Table 3). This result indicates that P removed in the crop was replaced by a combination of P applied in treatments and soil supply, in synchrony avoiding a decline in P Index despite significant P off-take. This occurred in the majority of P treatments with the exception of two treatments, the Ca$_1$- and Ca$_2$-DPS treated plots which fell within Index 4 compared to their starting point at Index 3. In contrary to other P treatments, Ca$_1$- and Ca$_2$-DPS treated plots showed a marked increase in Morgan's P (P$_m$) and a shift from P Index 3 ($P_m = 6.0-6.5$ mg L^{-1}) to P Index 4 ($P_m = 8.9-11.1$ mg L^{-1}). The reason of increase of P$_m$ with only Ca-type DPS is likely an artefact of the Morgan's P test, given that there was no difference in DM yield, P uptake and grass P concentrations, compared to other treatments. Supporting this idea of artefact is that the Mehlich-3 soil test results showed no corresponding increase (not significant) in soil test P (Figure 2 a and b). Morgan's P reagent has been shown to over-estimate plant available P in high Ca soils (Daly et al., 2015) where recalcitrant fractions of Ca-P are extracted by the reagent under high Ca conditions (Graca, 2018) therefore exaggerating the available pool.

No significant changes in pH, total carbon and organic carbon were observed (Table S1). The average concentrations of N, P, K, Mg and S in grass due to DPS treatment were in the range of 26.3−28.0, 3.0−3.3, 17.9−19.7, 2.0−2.1 and 3.3−3.4 mg g^{-1} DM, respectively, well within the requirement (Rigby and Smith, 2014) for perennial ryegrass (Table S2). These mineral concentrations in the grass harvested from DPS treatment plots were similar to those from mineral P applied plots.



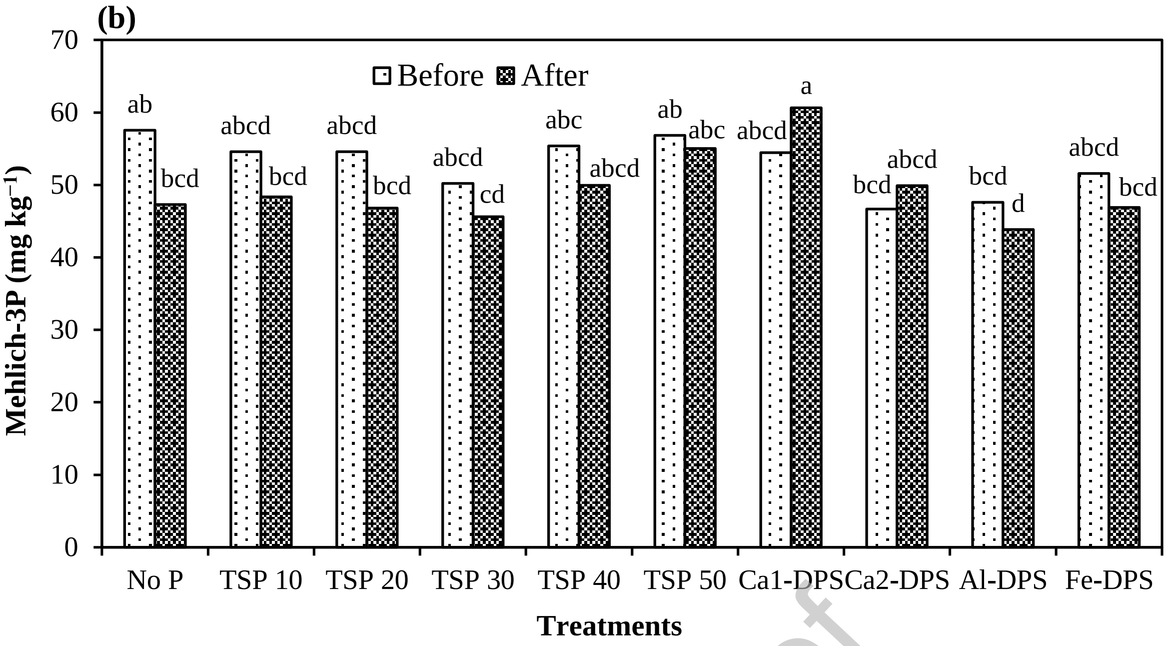


Figure 2 Pre- and post-harvest comparison of plant available (a) Morgan's P and (b) Mehlich-3P concentrations across treatments.

3.3 N availability and N-FRV

In N trial plots, DPS treatments showed significantly higher grass DM yield compared to the no N treatment in the 1st harvest with higher DM yield observed to be in the order of Ca_2-DPS > Fe-DPS > Al-DPS > Ca_1-DPS (Table 6). An increasing trend of DM yield was observed for the higher rate of mineral N fertiliser application in the 1st harvest. This means the experimental site was responsive to N application (Table 6). For the subsequent harvests (2nd to 4th), DM yield was not statistically different between treatments (Table 6) indicating little or no carryover N availability from either the mineral fertiliser or the DPS. In the 1st harvest, the grass N concentration was observed to be significantly higher for Ca_1-DPS treatment than the no N treatment, while Ca_2- and Fe-DPS treatments were not different compared to no N treatment except that Al-DPS showed significantly lower N concentration. The N concentrations in grass samples from 2nd to 4th harvests were statistically not different across all N treatments as well as in no N treatment. The exception here is the Fe-DPS treatment which showed significantly higher N concentration than the zero N treatment in the 2nd harvest (Table 7).

The N uptake due to Ca_1-, Ca_2- and Fe-DPS treatments applied at 60 kg-N ha^{-1} was significantly higher than the no N treatment in the 1st harvest, while it was similar (not significant) for Al-DPS and no N treatments (Table 8). The higher application rate of mineral N fertiliser provided higher N uptake. However, this trend was observed only for 1st harvest (Table 8). Based on the higher cumulative N uptake (kg N ha^{-1}) over 4 harvests the DPS samples can be ranked as Fe-DPS (161) > Ca_2-DPS (146) > Ca_1-DPS (145) > Al-DPS (137) in terms of N recovery, respectively. In comparison, the cumulative N uptake in plots receiving a mineral N fertiliser rate of 60 kg ha^{-1} was 185 and that of the zero N control plots was 132 kg N ha^{-1}, respectively. This level of N uptake from a zero N control is similar to the range of 102 to 153 kg N ha^{-1} reported by Forrestal et al. (2017) in Irish grassland trials indicating the trial site is representative of typical productive Irish agricultural soils. The first year apparent N recovery values for the mineral N fertiliser application rates (20–100 kg ha^{-1}) were observed between 59–103% where N 40 kg ha^{-1} showed the highest recovery value. DPS products at an application rate of 60 kg ha^{-1} showed lower apparent N recovery between 8 and 48% compared to 87% with a similar mineral N rate. Typically apparent N recovery values varied between 60–70% for mineral N application rates of 0–240 kg ha^{-1}, which are commonly found to be higher when compared with the N recovery of organic fertilizers (Rigby and Smith, 2014). For example, different types of industrial bio-waste based organic fertilisers such as dewatered mesophilic anaerobic digestate of municipal solid waste, digested biosolids (dewatered mesophilic), liquid thermophilic aerobic digestate of food waste (vegetable/bread/cooked meat) and liquid anaerobic codigestate of food, animal slurry and abattoir wastes were evaluated by Rigby and Smith (2014) for their N FRV in perennial ryegrass production from which the 1st year apparent N recovery values could be estimated to 8, 36, 56 and 57%, respectively. A number of factors such as type and source of organic fertilisers and their treatment conditions (e.g. undigested, digested, composting, drying temperature, storage period, lime treatment, etc.), C:N ratio, N mineralisation, application rate, soil texture and biological properties, soil temperature, moisture and pH can affect N transformations in organically-amended soil and results in variable apparent N recovery values for organic fertilisers (Rigby et al., 2016).

Table 6 Effect of treatment and rate on grass DM yield across 4 consecutive harvestings* between June − October 2017. Values indicated in brackets are standard deviations (n=4).

Treatment	N rate	Harvest			
		1	2	3	4
	kg ha^{-1}	DM yield (kg ha^{-1})			
No N	0	2434 ^{g}	1478 ^{a}	2641 ^{a}	288 ^{a}
		(241)	(526)	(174)	(134)
CAN	20	3417 ^{d}	1218 ^{a}	2451 ^{a}	327 ^{a}
		(671)	(315)	(359)	(68)
CAN	40	4288 ^{c}	1384 ^{a}	2523 ^{a}	413 ^{a}
		(418)	(292)	(289)	(56)
CAN	60	4946 ^{ab}	1199 ^{a}	2330 ^{a}	309 ^{a}
		(206)	(64)	(229)	(102)
CAN	80	4813 ^{b}	1197 ^{a}	2314 ^{a}	301 ^{a}
		(276)	(217)	(319)	(47)
CAN	100	5324 ^{a}	1379 ^{a}	2489 ^{a}	369 ^{a}
		(836)	(118)	(99)	(111)

Ca_1-DPS	60	2742 ^{f}	1100 ^{a}	2577 ^{a}	337 ^{a}
		(115)	(144)	(271)	(182)
Ca_2-DPS	60	3284 ^{de}	1284 ^{a}	2482 ^{a}	353 ^{a}
		(231)	(77)	(316)	(88)
Al-DPS	60	2978 ^{e}	1201 ^{a}	2670 ^{a}	399 ^{a}
		(340)	(249)	(152)	(78)
Fe-DPS	60	3074 ^{de}	1458 ^{a}	2569 ^{a}	388 ^{a}
		(410)	(221)	(152)	(136)

Mean comparison by *F*-protected LSD test ($P \leq 0.05$); Within columns shared letters denote no difference (p > 0.05), and unshared letters denote a statistical difference ($p \leq 0.05$); DPS: dairy processing sludge; Ca_1 and Ca_2-DPS: calcium-phosphorus rich lime treated sludge; Al-DPS: aluminium rich activated sludge; Fe-DPS: iron rich activated sludge; CAN: calcium ammonium nitrate; * Harvesting on 07/06/17, 18/07/17, 14/09/17, and 18/10/17.

Table 7 Effect of treatment and rate on grass N concentrations across 4 consecutive harvestings* between June − October 2017. Values indicated in brackets are standard deviations (n=4).

Treatment	N rate	Harvest			
		1	2	3	4
	kg ha^{-1}	N concentration (% of DM)			
No N	0	1.70 ^{b}	1.70 ^{b}	2.13 ^{a}	3.53 ^{a}
		(0.2)	(0.0)	(0.1)	(0.1)
CAN	20	1.70 ^{b}	1.75 ^{ab}	2.23 ^{a}	3.48 ^{a}
		(0.3)	(0.1)	(0.1)	(0.0)
CAN	40	1.80 ^{b}	1.78 ^{ab}	2.25 ^{a}	3.53 ^{a}
		(0.2)	(0.0)	(0.1)	(0.1)
CAN	60	2.08 ^{a}	1.78 ^{ab}	2.18 ^{a}	3.55 ^{a}
		(0.1)	(0.1)	(0.1)	(0.1)

CAN	80	2.05 ^{a}	1.75 ^{ab}	2.20 ^{a}	3.63 ^{a}
		(0.1)	(0.1)	(0.1)	(0.1)
CAN	100	2.18 ^{a}	1.83 ^{ab}	2.25 ^{a}	3.70 ^{a}
		(0.2)	(0.0)	(0.1)	(0.1)
Ca_1-DPS	60	2.00 ^{a}	1.83 ^{ab}	2.25 ^{a}	3.70 ^{a}
		(0.1)	(0.0)	(0.1)	(0.2)
Ca_2-DPS	60	1.70 ^{b}	1.78 ^{ab}	2.20 ^{a}	3.50 ^{a}
		(0.1)	(0.1)	(0.1)	(0.1)
Al-DPS	60	1.40 ^{c}	1.85 ^{ab}	2.30 ^{a}	3.65 ^{a}
		(0.9)	(0.1)	(0.1)	(0.1)
Fe-DPS	60	1.95 ^{ab}	1.98 ^{a}	2.28 ^{a}	3.60 ^{a}
		(0.0)	(0.2)	(0.1)	(0.1)

Mean comparison by *F*-protected LSD test ($P \leq 0.05$); Within columns shared letters denote no difference ($p > 0.05$), and unshared letters denote a statistical difference ($p \leq 0.05$); * Harvesting on 07/06/17, 18/07/17, 14/09/17, and 18/10/17.

Table 8 Effect of treatment and rate on grass N uptake across 4 consecutive harvestings* between June − October 2017. Values indicated in brackets are standard deviations (n=4).

Treatment	N rate	Harvest			
		1	2	3	4
	kg ha^{-1}	N uptake (kg N ha^{-1})			
No N	0	40.5 ^{g}	25.0 ^{a}	56.3 ^{ab}	10.3 ^{a}
		(3.3)	(9.1)	(5.8)	(4.8)
CAN	20	56 ^{d}	21.3 ^{a}	55.3 ^{ab}	11.3 ^{a}

		(11.1)	(6.1)	(9.3)	(2.3)
CAN	40	77.8^{c}	24.5^{a}	57.3^{ab}	14.3^{a}
		(7.0)	(5.5)	(7.1)	(2.2)
CAN	60	101.3^{b}	21.5^{a}	50.8^{b}	11.3^{a}
		(5.2)	(0.8)	(5.4)	(3.8)
CAN	80	98.3^{b}	25.3^{a}	51.0^{ab}	11.0^{a}
		(8.2)	(2.9)	(6.6)	(1.9)
CAN	100	115.8^{a}	20.5^{a}	58.8^{ab}	13.8^{a}
		(21.4)	(2.7)	(1.6)	(4.4)
Ca$_1$-DPS	60	54.5^{d}	20.1^{a}	57.5^{ab}	12.4^{a}
		(0.8)	(3.1)	(6.3)	(6.3)
Ca$_2$-DPS	60	56.2^{d}	23.1^{a}	54.5^{ab}	12.5^{a}
		(3.9)	(1.5)	(6.4)	(3.0)
Al-DPS	60	39.8^{g}	21.8^{a}	56.3^{ab}	14.3^{a}
		(26.8)	(5.1)	(5.6)	(2.4)
Fe-DPS	60	59.5^{d}	28.8^{a}	58.6^{a}	14.0^{a}
		(6.7)	(3.1)	(6.2)	(4.7)

Mean comparison by *F*-protected LSD test ($P \leq 0.05$); Within columns shared letters denote no difference ($p > 0.05$), and unshared letters denote a statistical difference ($p \leq 0.05$); * Harvesting on 07/06/17, 18/07/17, 14/09/17, and 18/10/17.

The cumulative N uptake obtained over 4 harvests was plotted against corresponding mineral N fertiliser application rate, which provided a strong positive linear correlation ($y = 0.7329x + 134.39$, $R^2=0.919$) between N uptake (y) and mineral N fertiliser rate (x) applied from 0 to 100 kg ha^{-1}. The N uptake due to DPS treatments was compared with the mineral N fertiliser response to calculate FRV as a percentage of total N applied as per eq. (1). This provided the N-FRV of DPS treatments as Fe-DPS 54%, Ca_2-DPS 25%, Ca_1-DPS 22% and Al-DPS 8%, respectively. These values are quite similar to the estimated apparent N recovery as shown in Table 9. According to eq. (2), the calculation of N FRV also provides closer values as to what was found using mineral N fertiliser response (Table 9). In comparison to N FRV of DPS treatments, the calculation of N replacement use efficiency (N-RUE) (as shown in Table 9) as per eq. (4) provides a relative N use efficiency of DPS with respect to a mineral fertiliser equivalent without considering a control (Sigurnjak et al., 2019).

The N FRV of tested DPS varied a great deal, indicating the importance of deriving these values so as to incorporate DPS into fertiliser programmes appropriately. Some of the common organic fertilisers (farmyard manure, slurries, crop residues) currently applied in many EU countries have large variation in N FRV values. For example, current national Action Programmes in the UK, Denmark and the Netherlands use N FRV values of 10, 45 and 30-60%, respectively for N availability in farmyard manure, and values of 45, 75 and 60-80% for pig slurry, respectively (Hijbeek et al., 2018). In Ireland, the N FRV of cattle slurry is recommended to be in the range between 15 to 40% depending on the application timing and method (Teagasc, 2016). Currently, there is no guideline value for N FRV of dairy processing sludge. This poses a great challenge to the dairy milk processing industry with respect to promotion of such bio-based fertilizers as valuable recyclable fertilisers. For the municipal wastewater treated sewage sludge derived biosolids, the recommendations of N FRV varies between 15 to 45% in the U.K. depending on the type and treatment process of biosolids, for example, 15% for composted biosolids, 20% for digested sludge cake, lime stabilized and thermally dried sludge, and 45% for digested liquid sludge, respectively (Defra, 2010; Rigby et al., 2016).

The mineralisable N fraction in different organic residues is a key determinant of quantifying plant available N and this can vary widely depending on the hydrolysis and biodegradation of organic matter, thus affect the release of NH_4-N (Rigby et al., 2016). The NH_4-N content in organic fertilisers is one of the major inorganic N forms, which can be directly absorbed by plant roots (Pierzynski et al., 2005). Therefore, it should be expected that the higher NH_4-N content of organic residue based fertilisers would likely provide more plant available N or higher N FRV. Although Al-DPS had the highest NH_4-N content (about 6% of total N), it showed the lowest N FRV among the four DPS tested. With Al-DPS higher content of organic matter (about 62% on a dry matter basis) indicates less microbiologically stabilized sludge which after application might likely to increase soil microbial activity to decompose most of the labile organic matter that was not stabilized by microbial digestion during sludge processing (Rigby et al., 2009). This process causes a delay in N mineralisation due to the short-term immobilisation of N, thus reducing N availability for initial plant uptake (Smith et al., 1998a). Moreover, unstabilised organic matter degradation on the soil surface causes N loss through gaseous emissions as ammonia (NH_3) is volatilised and denitrification occurs (Rigby et al., 2016). These facts can be attributed to the lowest N FRV of Al-DPS in this study. Studies with dewatered sewage sludge derived biosolids reported 68 – 81% of NH_3 volatilisation losses in the first week after surface application to soil (Robinson and Polglase, 2000).

With respect to municipal wastewater processing, the upstream wastewater and sludge treatment processes including the dewatering method and the associated storage period have been reported to affect the proportion of mineral and organic N in the biosolids, and thus the release of the available N pool in amended soil (Cogger et al., 2004; Smith, 2014; Rigby et al., 2016). For example, activated sludge tends to contain greater concentrations of total N and mineral N (mainly NH_4-N), and has a mean total and mineral N content of 4.4% DM and 8.1% TN, respectively, compared with 1.5% and 2.3% in lime treated biosolids (Rigby et al., 2016). This is associated with losses of NH_3 through increased pH, temperature or mechanical agitation during lime treatment. Likewise activated DPS samples have higher total N (Fe-DPS: 3.9%, Al-DPS: 4.3%) and NH_4-N (Fe-DPS: 4.9%, Al-DPS: 5.9%) content compared to lime treated DPS samples having total N (Ca_1-DPS: 3.7, Ca_2-DPS: 1.9%) and NH_4-N (Ca_1-DPS: 2.7, Ca_2-DPS: 2.6%), respectively, in the present study. The larger proportion of mineral N content in activated sludge compared to lime treated sludge corresponds well to the greater N FRV found with Fe-DPS. The exceptionally low N FRV of Al-DPS can be related to the poor sludge stabilization processes or the relative proportion of primary and activated sludge mixed together due to having much of the organic matter not been transformed or stabilized by microbial decomposition processes. The N FRV of Fe-DPS (activated sludge) and Ca-DPS (lime treated sludge) found in the present study (Table 9) correspond with the range of plant available N values reported in the literature for biosoilds, for example, 40–55% for dewatered aerobically digested biosolids and 37–41% for lime treated biosolids (Rigby et al., 2016).

Table 9 Cumulative N uptake, apparent N recovery, N replacement use efficiency (RUE) and N fertiliser replacement value (FRV) of tested DPS.

Treatment	N rate	Cumulative N uptake	Apparent N recovery	N RUE	N FRV from eq. (2)	N FRV from N response (eq. (1))
	kg ha^{-1}	kg ha^{-1}	%	%	%	%
Ca_1-DPS	60	145	21.7	78.4	23.3	21.9
Ca_2-DPS	60	146	23.3	78.9	26.4	24.9
Al-DPS	60	137	8.3	74.1	9.4	7.5
Fe-DPS	60	161	48.3	87.0	54.7	53.5

3.4 Future research needs

Future research should include a trial to determine P-FRV using low P index soil preferably. Further studies can be considered to assess influence of Ca, Al and Fe on plant available P on a range of soil types, to assess risk of environmental losses to air and water – for example, gaseous emission and nutrient runoff losses from DPS application to land, and to assess risk of metal and other emerging pollutants bio-accumulation to soil and crop tissue. In the recent laboratory based runoff simulation study, Ca-type DPS showed higher loss of dissolved reactive P compared to other DPS types (Al- and Fe-DPS) due to significant increase of P_m in Ca-DPS applied soils (Ashekuzzaman et al., 2020b). Field scale study using a rainfall simulator or natural rainfall is suggested to further investigate this P loss potential. Furthermore, future work is suggested to include alternative P extracting methods such as sodium bicarbonate ($NaHCO_3$) extractable-P (Olsen-P), in addition to Morgan's reagent, so that confounding factors that mask available P values can be observed. When dealing with high Ca and Al dairy sludges, the $NaHCO_3$ extractant (Olsen P test, Olsen et al., 1954) might be better suited to elucidate plant available P in soil with neutral and slightly acidic pH 6 to 7. The reason is this test can remove Ca-phosphates and phosphate adsorbed on surfaces of calcium and magnesium carbonates along with Al-phosphates (USDA, 2020). Moreover, research should also focus on using DPS or other bio-based products in an integrated fertiliser application programme which provides an option for balanced application of bio-based and chemical fertilisers to meet the demand of required crop nutrients like N, P, K and S. In this way a farmer can be given sound advice pertaining to the sustainable use of these industrial by-products converting them from a waste into an alternative organic fertiliser.

4. Conclusions

An agronomic trial in grassland micro-plots (8×2 m^2) with four representative dairy processing sludge (two activated sludge - Al-DPS and Fe-DPS, and two lime-stabilised sludge - Ca_1- and Ca_2-DPS) showed that grass dry matter yield and P uptake were statistically similar to mineral P fertiliser in a site at optimal soil P fertility indicating no negative impact of Ca, Al or Fe DPS on plant P uptake. As the experimental site was non-responsive to increasing mineral P rate it was not appropriate to derive a P FRV of DPS. Further study is suggested to investigate P FRV in low P concentration soil. Results from the N experiment showed a strong response to N application with significantly higher grass dry matter yield and N uptake for Fe and both Ca-type DPS applied plots compared to the control plots during the first harvest. The N FRV of DPS samples was observed to be between 8 to 54% with greater promise of N fertilizer efficiency of Fe and Ca-type DPS compared to the Al type. The significant increase of Morgan's soil test P was observed in Ca-type sludge applied plots was not supported by the results of the Melhich-3 test which showed no such change indicating that soil test results from land receiving this material should be interpreted with care. The findings therefore suggest DPS can be applied at a maintenance P fertiliser application rate in soil with an optimum P levels but long-term investigation is required to monitor soil P build up and any subsequent runoff P losses. The wide range of N FRV between activated and lime treated DPS types indicates the influence of upstream wastewater and sludge treatment processing on plant available N, an important finding for their appropriate incorporation into fertiliser programmes.

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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References

Ashekuzzaman, S.M., Forrestal, P., Richards, K., Fenton, O., 2019. 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., 2020a. Novel use of dairy processing sludge derived pyrogenic char (DPS-PC) to remove phosphorus in discharge effluents. Waste Biomass Valor. 11, 1453–1465.

Ashekuzzaman, S.M., Forrestal, P., Richards, K., Fenton, O., 2020b. Potential loss of nutrients, carbon and metals in simulated runoff associated with dairy processing sludge application. Int. J. Environ. Sci. Technol. https://doi.org/10.1007/s13762-020-02768-z

Atallah, E., Zeaiter, J., Ahmad, M.N., Kwapinska, M., Leahy, J.J., Kwapinski, W., 2020. The effect of temperature, residence time, and water-sludge ratio on hydrothermal carbonization of DAF dairy sludge. J. Environ. Chem. Eng. 8, 103599.

Bernal, M.P., 2017. Grand challenges in waste management in agroecosystems. Front. Sustain. Food Syst. 1, 1. https://doi.org/10.3389/fsufs.2017.00001.

Börjesson, G., Kirchmann, H., Katterer, T., 2014. Four Swedish long-term field experiments with sewage sludge reveal a limited effect on soil microbes and on metal uptake by crops. J Soils Sediments 14,164–177.

Börjesson, G., Kätterer, T., 2018. Soil fertility effects of repeated application of sewage sludge in two 30-year-old field experiments. Nutr. Cycl. Agroecosyst. 112, 369–385.

Brennan, R.B., Fenton, O., Grant, J., Healy, M.G., 2011. Impact of chemical amendment of dairy cattle slurry on phosphorus, suspended sediment and metal loss to runof from a grassland soil. Sci. Total Environ. 409, 5111–5118.

Brown, J.R., Bough, W.A., Hoenshell, C., 1990. Use of lime-stabilized dairy-plant waste for forage production. J. Prod. Agric. 3(3), 340–4.

Cogger, C.G., Bary, A.I., Sullivan, D.M., Myhre, E.A., 2004. Biosolids processing effects on first- and second-year available nitrogen. Soil Sci. Soc. Am. J. 68, 162–167.

Daly, K., Casey, A., 2003. Eutrophication from agricultural sources: environmental soil phosphorus test. EPA Research Report, ISBN: 1-84095-111-7, Environmental Protection Agency, Ireland.

Daly, K., Styles, D., Lalor, S., Wall, D., 2015. Phosphorus sorption, supply potential and availability in soils with contrasting parent material and soil chemical properties. Eur. J. Soil Sci. 66, 792–801.

Defra, 2010. Fertilizer Manual (RB209). eighth ed. The Stationery Office, Norwich.

Delin, S., 2011. Fertilizer value of nitrogen in hen and broiler manure after application to spring barley using different application timing. Soil Use Manage. 27, 415–426.

Delin, S., 2016. Fertilizer value of phosphorus in different residues. Soil Use Manage. 32, 17–26.

EC (European Commission), 2015. Factsheet: An ambitious EU circular economy package. Available at: https://ec.europa.eu/commission/sites/beta-political/files/circular-economy-factsheet-general_en.pdf (accessed 27 April 2020).

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.

Forrestal, P.J., Harty, M.A., Carolan, R., Watson, C.J., Lanigan, G.J., Wall, D.P., Hennessy, D., Richards, K.G., 2017. Can the agronomic performance of urea equal calcium ammonium nitrate across nitrogen rates in temperate grassland? Soil Use Manage. 33, 243–251.

EU (European Union), 2019. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 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. Official Journal of the European Union, L 170, 62, pg-1.

Fehily Timoney and Company, 1999. Codes of good practice for the use of biosolids in agriculture-guidelines for farmer. https://www.housing.gov.ie/sites/default/files/migrated-files/en/Publications/Environment/Water/FileDownLoad%2C17228%2Cen.pdf.

Foster, P., 2006. The Production of Vermicompost from Dairy Sludge and its Value as a Plant Growth Medium. MSc Thesis, Institute of Technology, Sligo, Ireland. Weblink (accessed on 15/11/2020): file:///C:/Users/sm.ashekuzzaman/Downloads/Foster_MSc_Thesis.pdf

Graca, J., (PhD dissertation) 2018. An Evaluation of Phosphorus Supply Capacities in Irish Grassland Soils. University of Limerick, Ireland.

Hijbeek, R., ten Berge, H.F.M., Whitmore, A.P., Barkusky, D., Schroder, J.J., van Ittersum, M.K., 2018. Nitrogen fertiliser replacement values for organic amendments appear to increase with N application rates. Nutr. Cycl. Agroecosyst. 110, 105–115.

Ketterings, Q.M., Czymmek, K.J., 2002. Phosphorus Soil Testing and Nutrient Management Planning in New York. "What' Cropping Up?" 12 (4): 1-3. Weblink (accessed on 15/11/2020): http://nmsp.cals.cornell.edu/publications/extension/recentdevelsoiltest.pdf

Khiari, L., Joseph, C-A., Gallichand, J., Beecher, N., Bouslama, S., 2020. “Classification and Assessment Models of First Year Biosolids Phosphorus Bioavailability.” Waste Biomass Valor. 11, 1443-1452.

Kwapinska, M., Horvat, A., Liu, Y., Leahy, J.J., 2020. Pilot scale pyrolysis of activated sludge waste from milk processing factory. Waste Biomass Valor. 11, 2887–2903.

Lalor, S.T.J., Schröder, J.J., Lantinga, E.A., Oenema,O., Kirwan,L., Schulte, R.P.O., 2010. Nitrogen Fertilizer Replacement Value of Cattle Slurry in Grassland as Affected by Method and Timing of Application. J. Environ. Qual. 40(2), 362-73.

Lopez-Mosquera, M.E., Cascallana, V., Seoane, S., 2002. Comparison of the effects of dairy sludge and a mineral NPK fertilizer on an acid soil. Invest. Agrar. Prod. Prot. Veg. 17, 87-99.

López-Mosquera, M.E., Moirón, C., Carral, E., 2000. Use of dairy-industry sludge as fertiliser for grasslands in northwest Spain: heavy metal levels in the soil and plants. Resour Conserv. Recy. 30(2), 95-109.

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, 1464–1475.

Mehlich, A., 1984. Mehlich 3 soil test extractant: a modiication of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15, 1409–1416.

Morgan, M.F., 1941. Chemical soil diagnosis by the universal soil testing system. Connecticut Agricultural Experiment Station, Bulletin 450. Website link (Accessed 17/05/2020): https://portal.ct.gov/-/media/CAES/DOCUMENTS/Publications/Bulletins/B450pdf.pdf?la=en

Nicholson, F., Boghal, A., Taylor, M., McGrath, S. P., Withers, P. 2018. Long-term effects of biosolids on soil quality and fertility. Soil Science 183 (3), 89-98.

Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S. Dep. of Agric. Circ. 939.

Pierzynski, G.M., Sims, J.T., Vance, G.F., 2005. Soils and Environmental Quality. CRC Press, Taylor & Francis Group, Boca Raton.

Plunkett, M., Wall, D., 2016. Making best use of cattle slurry N, P and K. Forage and Nutrition Guide, Dublin, Ireland. Website link (Accessed on 17/05/2020): https://www.slideshare.net/LiamDePaor/forage-guide-2016-64169957

Rigby, H., Smith, S.R., 2014. The nitrogen fertiliser value and other agronomic benefits of industrial biowastes. Nutrient Cycl. Agroecosyst. 98, 137-154.

Rigby, H., Clarke, B.O., Pritchard, D.L., et al., 2016. A critical review of nitrogen mineralization in biosolids-amended soil, the associated fertilizer value for crop production and potential for emissions to the environment. Science Total Environ. 541, 1310-1338.

Rigby, H., Perez-Viana, F., Cass, J., Rogers, M., Smith, S.R., 2009. The influence of soil and biosolids type, and microbial immobilisation on nitrogen availability in biosolids amended agricultural soils — implications for fertilizer recommendations. Soil Use Manag. 25, 395–408.

Robinson, M.B., Polglase, P.J., 2000. Volatilization of nitrogen from dewatered biosolids. J. Environ. Qual. 29, 1351.

Ryan, M.P.,Walsh, G., 2016. The Characterisation of DairyWaste and the Potential of Whey for Industrial Fermentation. EPA Research Report, Environmental Protection Agency, Ireland.

Sigurnjak, I., Brienza, C., Snauwaert, E., De Dobbelaere, A., De Mey, J., Vaneeckhaute, C., Michels, E., Schoumans, O., Adani, F., Meers, E., 2019. Production and performance of bio-based mineral fertilizers from agricultural waste using ammonia (stripping-) scrubbing technology. Waste Manag. 89, 265-274.

Smith, S.R., 2014. How activated sludge has been transformed from a waste to a resource, and the implications of this for the future of the activated sludge process. In: Horan, N.J. (Ed.), Activated Sludge: Past, Present and Future. CIWEM(Chartered Institution of Water and Environmental Management), London.

Smith, S.R., Woods, V., Evans, T.D., 1998. Nitrate dynamics in biosolids-treated soils. I. Influence of biosolids type and soil type. Bioresour. Technol. 66, 139–149.

Sullivan, D.M., Cogger, C.G., Bary, A.I., 2015. Fertilising with biosolids. A Pacific North west Extension Publication, Oregon State University, Washington State University, University of Idaho. Website link (accessed on 17/05/2020): https://catalog.extension.oregonstate.edu/sites/catalog/files/project/pdf/pnw508_0.pdf

Teagasc Greenbook, 2016. Major and micro nutrient advice for productive agricultural crops. In: Johnstown Castle Wall DP, Plunkett M (eds) (Wexford: Teagasc; Environment Research Centre), p 81.

USEPA, 1996. SW-846 Test Method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices. United States Environmental Protection Agency.

USDA (United States Department of Agriculture), 2020. Selection of an appropriate phosphorus test for soils. Soil Survey Laboratory, National Soil Survey Center, Lincoln. Weblink (accessed on 15/11/2020): https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_051918.pdf

Vanden Nest, T., Amery, F., Fryda, L., Boogaerts, C., Bilbao, J., Vandecasteele, B., 2021. Renewable P sources: P use efficiency of digestate, processed animal manure, compost, biochar and struvite. Sci Total Environ. 750. https://doi.org/10.1016/j.scitotenv.2020.141699.

Wendling, L.A., Blomberg, P., Sarlin, T., Priha, O., Arnold, M., 2013. Phosphorus sorption and recovery using mineral-based materials: Sorption mechanisms and potential phytoavailability. Appl. Geochem. 37, 157–169.