



Phosphorus and nitrogen leaching from an organic and a mineral soil receiving single and split dairy slurry applications: a laboratory column experiment

J. L. González Jiménez¹ · K. Daly² · M. G. Healy³

Received: 4 July 2022 / Accepted: 31 October 2022

© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2022

Abstract

Purpose Intensification of farming means that organic soils, of low phosphorus (P) holding capacity, are being brought into production. Consequently, farmers may have to adjust their fertiliser application regimes to reduce environmental risk. The aim of this paper is to test the hypothesis that overall loads of P and nitrogen are smaller when applications are split in two compared to a single application.

Materials and methods A laboratory column experiment was conducted in which two soils, one organic and one mineral, were exposed to dairy slurry applications of 15, 30 and 55 kg P ha⁻¹ applied in one single application or split into two applications. The columns were uniformly irrigated weekly with 160 mL of distilled water (equivalent to average precipitation in Ireland) and the leached water was analysed for nutrients.

Results and discussion There were no significant cumulative P loads in the leached water for any soil type or treatment (minimum and maximum values ranging from 0.04 to 0.12 kg dissolved reactive phosphorus (DRP) ha⁻¹ and 0.09 to 0.14 kg DRP ha⁻¹ for the organic and mineral soil, respectively, and 1.5 to 1.8 kg total phosphorus (TP) ha⁻¹ and 1.8 to 2.9 kg TP ha⁻¹ for the organic and mineral soil, respectively). There was high ammonium-N retention within the organic soil (0.2–0.4 kg ha⁻¹, compared to 15.0–36.8 ha⁻¹ for mineral soils in the leached water). Nitrate-N loads were higher from the organic soil (6.5–105.3 ha⁻¹) than the mineral soil (9.7–17.4 ha⁻¹), although for both soils, loads from the amended columns were lower than the controls (110.7 and 20.1 NO₃-N ha⁻¹ for the organic and mineral soil, respectively).

Conclusions The overall finding of this study was that split slurry applications had little effect on nutrient exports when compared to single applications, making the amounts of slurry applied, and not the application regime, the predominant factor in nutrient loss.

Keywords Phosphorus · Nitrogen · Leaching · Organic soil · Mineral soil

Responsible editor: Weixin Ding

✉ M. G. Healy
mark.healy@universityofgalway.ie

¹ Department of Forest Mycology and Plant Pathology, Faculty of Natural Resources and Agricultural Sciences, Swedish University of Agricultural Sciences, Uppsala, Sweden

² Teagasc, Johnstown Castle, Environment Research Centre, Co., Wexford, Republic of Ireland

³ Civil Engineering and Ryan Institute, University of Galway, Co., Galway, Republic of Ireland

1 Introduction

Land application of animal-derived manures such as dairy slurry is a common practice to improve soil fertility, but it may also pose a risk of phosphorus (P) and nitrogen (N) losses to the surrounding waters (Wang et al. 2019). Although surface runoff is considered to be the main pathway of nutrient losses from fertiliser applications, especially followed by rainfall events, leachate or subsurface processes may also play an important role in these incidental, diffuse transfers of P and N from agricultural soils to waters (Hart et al. 2004).

With intensification of agricultural practices across Europe, marginal soils such as peat soils and other peat-derived soils are being cultivated to meet food demands. Organic soils have low P retention properties due to intense competition reactions of organic acids for the scarce cationic sorption sites of the mineral fraction (Gerke 2010). Moreover, organic soils have a low bulk density and can develop significant preferential subsurface flow pathways due to their high hydrophobicity when they are exposed to drying and wetting processes (Riddle et al. 2018; Simmonds et al. 2017).

Organic soils account for approximately 7% of the total land area in Europe, of which the Scandinavian countries and north-west Europe are among the countries with the highest representation of these soils in their territories. Different management strategies to mitigate P transport from the source to the surrounding water bodies have been proposed, such as environmental soil P testing, matching P applications with crop requirements and timing of fertilisation to avoid the concurrence of elevated moist soil conditions with fertiliser applications (Macintosh et al. 2018). Similarly, various strategies have been employed to reduce N leaching and runoff such as reduced N fertilisation (Constantin et al. 2010). Smaller, but more frequent applications, of fertiliser has been proposed as a measure to reduce P exports from the soil in temperate regions where frequent rainfalls are likely to occur throughout the whole year (González Jiménez et al. 2019). However, few studies have been conducted in organic soils receiving frequent but smaller fertiliser applications, and the potential impact of subsurface transfer of P and N in these soils under this management strategy remains poorly understood.

The hypothesis of this paper is that soils with elevated organic matter (OM) content have higher P and N loads in leached water than mineral soils when dairy slurry is applied. Therefore, the aim was to examine losses of P and N in leached water from a laboratory-scale column experiment following single and split applications of dairy slurry at different doses to soils of contrasting OM content. To test this hypothesis and address the study objectives, a laboratory leachate column experiment was conducted. Three rates of dairy slurry were applied in one single dose and in split doses on disturbed soil columns containing either a mineral or organic soil.

2 Materials and methods

2.1 Soil collection and analysis

Organic and mineral soils were collected from two dry-stock farms located in a “high status” catchment in the south east of Ireland (52° 17'N, 6° 29'W). Approximately 150 kg of each soil type was collected from the top 0.2 m, air-dried, manually sieved to pass a 2 mm sieve, and thoroughly

mixed. A subsample from each soil type was analysed for physico-chemical properties. At the time of soil collection, intact soil cores ($n=3$) were taken to determine fresh bulk density and gravimetric water content, according to British standards (BS 1377-2 1990).

Cation exchange capacity (CEC) was estimated using the method described by Ross (1995). pH (1:1 in H₂O) was determined according to McLean (1982). Total OM was determined using the loss on ignition test at 360 °C (Schulte and Hopkins 1996). Total C and N were estimated by combustion (McGeehan and Naylor 1988). Total and plant available P were determined by the acid perchloric digestion (Sommers and Nelson 1972) and the Morgan's P test (Morgan, 1941) procedures, respectively. Particle size analysis was determined using the hydrometer method (ASTMD 2002). The Mehlich-3 soil test was used to determine extractable aluminium (Al), calcium (Ca), iron (Fe) and P (Mehlich 1984). As a measure of the degree of P saturation of the soils, the P saturation ratio (PSR) for acidic soils was calculated using:

$$[P/(Al + \gamma * Fe)]_{Mehlich-3} \quad (1)$$

where P, Al and Fe are Mehlich-3 extractable forms on a molar basis and γ is a weighing factor, set at 1 for the mineral soil and 5 for the organic soil, to compensate for the low extraction efficiency of Fe in organic soils (Guérin et al. 2007).

Additionally, P sorption isotherm experiments were conducted to determine the total sorption and bonding capacities of both soils. Twenty-five millilitres of varying concentrations (0, 5, 10, 30 and 60 mg P L⁻¹) of a KH₂PO₄ stock solution was added to 50 mL polyethylene centrifuge tubes each containing 1 g of soil ($n=3$). Samples were shaken for 24 h at 250 rpm in a reciprocating shaker, allowed to settle for 1 h and filtered through a 0.45 µm membrane filter, and the filtrate was analysed for dissolved reactive phosphorus (DRP) using a nutrient analyser (Konelab 20, Thermo Clinical Lab systems, Finland). A linearised Langmuir adsorption equation (Kovar and Pierzynski 2009) was used to fit the data:

$$\frac{C}{S} = \frac{1}{kS_{max}} + \frac{C}{S_{max}} \quad (2)$$

where C is the concentration of P after equilibration (in mg L⁻¹) and S is the total amount of P retained (mg kg⁻¹), S_{max} represents the maximum amount of P that can be sorbed by the soil (mg kg⁻¹), and k is a constant related to the bond strength of added P to soil (L mg⁻¹ P).

2.2 Slurry collection and analysis

Dairy slurry was collected in one 20 L capacity drum from the Teagasc Agricultural Research Centre, Moorepark,

Fermoy, Co. Cork, and kept refrigerated (10 ± 1 °C) prior to the start of the experiment. Homogenised subsamples were tested in triplicate for total P (TP), total N (TN), DRP, ammonium (NH_4), pH and dry matter (DM). Total P and TN were measured using acid persulfate digestion and by combustion oxidation, respectively. Dry matter was measured by drying at 105°C for 24 h and pH was determined using a pH probe (WTW). A subsample of fresh slurry was centrifuged before being filtered ($0.45\ \mu\text{m}$) and analysed for DRP and NH_4 . All the parameters were determined using the standard methods (APHA 2005).

2.3 Soil columns setup

Prior to placement in the columns, the gravimetric water content of the two soils was modified using distilled water to attain the same value as that measured at the time of sampling. The soil was packed in forty-two 0.3-m deep and 0.104-m internal diameter PVC columns (21 for each soil type), each with perforated bases to allow free drainage. A 0.05-m layer of gravel was placed at the bottom of the columns, which was overlain by 0.2 m of soil, compacted in 0.05 m depth intervals, to attain the same fresh bulk density as obtained in the field. At each depth interval, the soil was pressed against the column to avoid the occurrence of preferential flow paths. Re-packed soil columns are commonly used in research studies (Hou et al. 2018; Mazloomi and Jalali 2019; Miri et al. 2022). Although intact, undisturbed soil columns are preferable, compression of the soil (and, in particular, organic soils) is probable without specialised equipment. Therefore, re-packed soil columns, in which the soil is allowed adequate time to consolidate before the experiment begins, are used.

The experiment was conducted in a temperature ($10 \pm 1^\circ\text{C}$)- and humidity ($85 \pm 8\%$)-controlled room, representative of average climatic conditions in Ireland (Walsh 2012). Each column was irrigated weekly with 160 mL of distilled water, and applied homogeneously onto the surface in two aliquots each of 80 mL over a 2 h period. This rate of water addition was representative of the yearly average precipitation in Ireland (19 mm per week, 988 mm per year; Walsh 2012). Distilled water was used to ensure consistency in water chemistry, as the chemistry of rainwater changes over time due to anthropogenic and terrestrial effects (Keresztesi et al., 2020). Prior to the start of the experiment, the columns were allowed to incubate for a period of 16 weeks to stabilise the pulse in N mineralisation following drying and wetting processes in the soil.

The treatments (each at $n=3$) examined were as follows: (1) one single application of $15\ \text{kg P ha}^{-1}$ ($11.8\ \text{mg P column}^{-1}$), (2) a $15\ \text{kg P ha}^{-1}$ applied in two split applications of $7.5\ \text{kg P ha}^{-1}$ ($5.9\ \text{mg P column}^{-1}$) each, (3) one single application of $30\ \text{kg P ha}^{-1}$ ($23.6\ \text{mg P column}^{-1}$),

(4) a $30\ \text{kg P ha}^{-1}$ applied in two split applications of $15\ \text{kg P ha}^{-1}$ ($11.8\ \text{mg P column}^{-1}$) each, (5) one single application of $55\ \text{kg P ha}^{-1}$ ($43.2\ \text{mg P column}^{-1}$), (6) $55\ \text{kg P ha}^{-1}$ applied in two split applications of $27.5\ \text{kg P ha}^{-1}$ ($21.6\ \text{mg P column}^{-1}$) each and (7) a study control (soil only). Based on the content of TP of the dairy slurry, the amounts of slurry applied were 36, 72 and 132 g for the single 15, 30 and $55\ \text{kg ha}^{-1}$, respectively, and 18, 36 and 66 g for the split applications. The amount of TN added was 64.6, 129.2 and $236.9\ \text{kg ha}^{-1}$ for applications of 15, 30 and $55\ \text{kg P ha}^{-1}$, respectively. The duration of the experiment was 34 weeks.

Single applications were made after the incubation period, at week 17, and split applications on week 17 and 25, respectively. The doses were selected based on current fertiliser recommendations on organic soils in Ireland, where the maximum allowance for P is $30\ \text{kg P ha}^{-1}$, depending on the stocking rate and/or grazing regime (Wall and Plunkett 2020). However, a recent survey of farms with these soil types reported that the actual P applied may be up to 1.5 times higher than the advised amounts for organic soils (Roberts et al. 2017).

2.4 Leachate collection and analysis

Leached water was collected in plastic containers using funnels placed beneath each column. Volumes of leached water were measured and homogenised before subsampling. Unfiltered subsamples were analysed for TP using a Biotector Analyser (Biotector Analytical Systems Ltd.) and the pH was measured using a pH probe (WTW). Filtered subsamples ($0.45\text{-}\mu\text{m}$ pore size) were analysed for DRP, $\text{NH}_4\text{-N}$, total oxidised nitrogen (TON) and nitrite-N ($\text{NO}_2\text{-N}$) using a nutrient analyser (Konelab 20, Thermo Clinical Laboratories Systems, Finland) and total dissolved P (TDP) using a Biotector analyser (Biotector Analytical Systems Ltd.). Nitrate-N ($\text{NO}_3\text{-N}$) was calculated as the difference between TON and $\text{NO}_2\text{-N}$; dissolved unreactive P (DUP) as the difference between TDP and DRP; and total particulate P (TPP) as the difference between TP and TDP (APHA 2005; Murnane et al. 2018).

2.5 Data analysis

Each week, the cumulative mass of leached water from every column was measured and tested for the water quality parameters of interest. This enabled the mass release from each column to be measured and expressed as a loss per unit surface area of each column. Each cumulative curve was fitted using a 3-parameter logistic function. In addition, a 95% confidence band was calculated using the delta method and added to each of the curves to express uncertainty in the estimates. The regression analyses were performed following the non-linear least squares method using R statistical software. These data were then extrapolated to produce a weekly gravimetric loss

per hectare (kg ha^{-1}) for each treatment. Additionally, in order to estimate the percentage of the nutrients applied that was released in the leached water, a mass balance was estimated for P and N as the difference between the cumulative losses of each nutrient and the control soil divided by the amount of the nutrient applied at each slurry treatment. Despite the repeated nature of the measurements, the use of the maximum (total) cumulative values of each nutrient as a single meaningful measure reduced the multivariate response to an univariate response, thus enabling the use of classical analysis methods (Davis 2002). The data were subjected to normality using a Shapiro–Wilk test and homogeneity of variance using Levine’s test. Differences in the loads in leachate (kg ha^{-1}) within and between factors (soil type and slurry application) were evaluated using a two-way (model 2) ANOVA, and simple effect analyses were performed by the Bonferroni test at $\alpha=0.05$ when the main and/or interaction effects were significant ($p<0.05$). Data analyses were performed in SPSS (IBM SPSS 24 Core Systems) using the GLM-Univariate procedure.

3 Results and discussion

3.1 Soil and slurry characteristics

Table 1 shows selected physical and chemical properties of both soils and their Langmuir equation parameters. The

organic and mineral soils were classified as a humic lithosol and typical brown earth, respectively, under the Irish soil classification system (Creamer et al. 2014), whose equivalents to the FAO soil classification system (IUSS Working Group WRB 2014) are lithic leptosol and haplic phaeozem. The organic soil had nearly seven times more OM content than the mineral soil, although the Mehlich-3 extractable Ca was slightly lower, yielding a moderately acidic pH for the former (5.5) and near to neutral pH for the latter (6.3). The P sorption ability (S_{max}) of the organic soil (1278 mg kg^{-1}) was higher than in the mineral soil (896 mg kg^{-1}), whilst the constant k , related to the bonding energy of added P to soil sorption sites, was similar in both soils (Table 1). The lower S_{max} of the mineral soil may have been partly attributable to its higher pH compared to the organic soil. pH has been shown to be inversely related to the S_{max} due to the alteration of the forms of P-fixing compounds such as clays and Al and Fe oxides that lead to desorption processes; lower soil pH favours the presence of free iron and aluminium oxides in soil matrix, whereas higher pH (6.5–7.5) exerts an opposite effect, lowering the concentration of free iron and aluminium oxides (Roy and De Datta 1985). However, it is likely that the main reason for the higher P sorption ability of the organic soil over the mineral soil is due to the activation of new sorption sites that were occluded by the native OM of the soil by the breaking of the soil structure when it was sieved prior packing in the columns, as it will be explained in the next subsection.

Table 1 Selected physico-chemical characteristics (standard deviations) of the two soils used in this study

Soil properties		Soil type	
		Organic	Mineral
pH		5.5 (0.3)	6.3 (0.1)
OM	g kg^{-1}	54.1 (2.1)	8.0 (0.2)
Dry bulk density	g cm^{-3}	0.41 (0.1)	0.99 (0.1)
Particle size			
Clay	%	13.9 (1.5)	16.9 (1.3)
Silt	%	27.3 (1.6)	37.4 (0.3)
Sand	%	58.8 (0.5)	45.7 (1.0)
Texture (USDA)		Sandy loam	Loam
Total C	mg kg^{-1}	276.8 (7.7)	39.2 (4.1)
Total N	mg kg^{-1}	16.5 (0.1)	3.6 (0.5)
Total P	mg kg^{-1}	884.0 (39.5)	770.0 (60.1)
Mehlich-3			
P	mg kg^{-1}	29.3 (3.1)	72.3 (3.1)
Al	mg kg^{-1}	328.7 (79.6)	591.7 (15.6)
Fe	mg kg^{-1}	350.7 (46.5)	334.0 (22.6)
Ca	mg kg^{-1}	2831.7 (51.7)	3042.0 (289.1)
Cation exchange capacity	cmol kg^{-1}	32.4 (5.6)	17.5 (0.2)
Phosphorus saturation ratio		0.022 (0.001)	0.084 (0.002)
Langmuir parameters			
Maximum adsorption capacity, S_{max}	mg kg^{-1}	1278.9	896.5
Bonding energy, k	$\text{m}^3 \text{g}^{-1}$	0.09	0.12

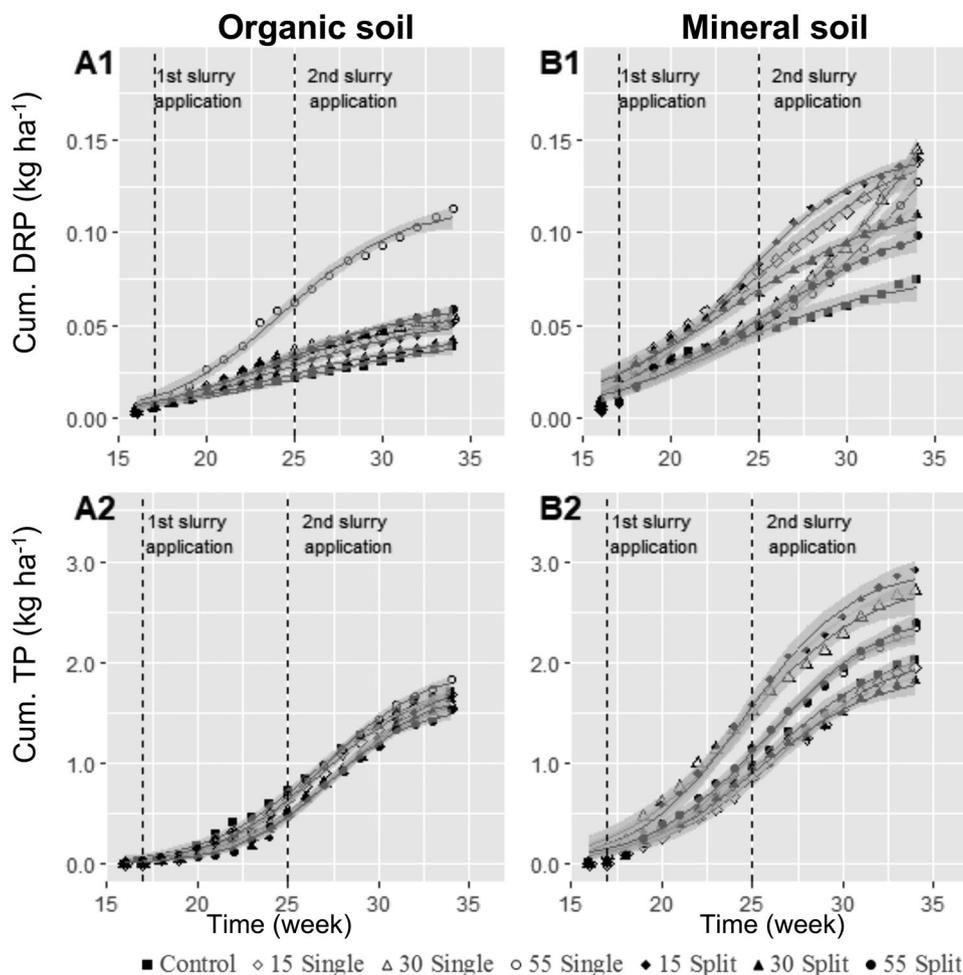
Mehlich-3 extractable P concentrations were low to optimum for the organic soil (29.3 mg kg^{-1}) with respect to agronomic recommendations (Mallarino et al. 2013) and very high for the mineral soil (72.3 mg kg^{-1}), possibly due to excessive fertiliser applications in the years prior to sample collection. The PSR of the mineral soil (0.084) was above the critical threshold of 0.05, indicating a potential source of P losses (Guérin et al. 2007). Despite S_{max} in the organic soil being higher than in the mineral soil, the degree of P saturation (as measured by the PSR) was more elevated for the latter, indicating that P was less strongly retained by the mineral soil (Beauchemin and Simard 1999). This seems to be in contradiction with the k values obtained from the Langmuir equation, where mineral soil had a slightly higher bonding energy compared to the organic soil (Table 1). As defined in Eq. (2), k is a constant derived from the sorption isotherms where increasing amounts of P are added to the soil, thus reflecting the overall binding energy across all the saturation process derived from the sorption isotherm trials. However, this constant may not necessarily reflect the binding energy of P to the soil at a specific, intermediate phase of the saturation process.

The ratio of TP to DRP in the dairy slurry was approximately 11:1, which implies that most of the P in the slurry was in the form of TPP and/or DUP. A low concentration of soluble P relative to the total P in dairy cattle slurry has been observed elsewhere (Brennan et al. 2014, 2011).

3.2 Phosphorus in leachate

Considering the organic soil, with the exception of the single application of 55 kg ha^{-1} (Fig. 1—A1), there was no statistically significant difference ($p > 0.05$) in the mass of DRP released between the slurry treatments and the study control. Similarly, there were no statistically significant differences in the DRP mass released across all treatments from the mineral soil (Fig. 1—B1). Comparing the mass of DRP released from both soils when subjected to the same application rate, there were no statistically significant differences for the control, single 55 and split 55 kg ha^{-1} applications ($p > 0.05$), suggesting that DRP losses in the leachate at these slurry applications (no slurry application in the case of the control) were of the same magnitude for both soils. However, mineral soil had significantly higher DRP releases in the single 15,

Fig. 1 Average cumulative leaching of dissolved reactive P (DRP) and total P (TP) for each treatment and soil type. Fitted lines represent a 3-parameter logistic model with 95% confidence intervals (CI). Dashed lines indicate slurry application times (week 17 and week 25)



single 30, split 15 and split 30 kg ha⁻¹ treatments than the equivalent treatments in the organic soil.

With regard to TP, treatment had no impact on the mass release from the organic soil (Fig. 1—A2), whereas there were significant differences between the control and the single 30 and single 55 kg ha⁻¹ treatments in the mineral soil (Fig. 1—B2). In general, the amounts of P losses observed in this study are somewhat lower than other similar leachate studies in which undisturbed organic and mineral soil columns were used. For example, Parvage et al. (2015) reported TP losses of 6.72 kg ha⁻¹ after 3 days of continuous leachate from peat soil columns receiving 22 kg P ha⁻¹ in the form of composted horse manure. In comparison, TP losses in the current study were lower than 2 kg ha⁻¹ after a much longer period of 19 weeks. Despite the higher S_{max} of the organic soil compared to the mineral soil in this experiment, the maximum amount of P that can be retained by each soil is higher for the mineral soil than for the organic soil due to the higher bulk density of the mineral soil compared to the organic soils. Thus, for the organic soil, the proportion of P applied in the slurry was 1.94, 3.88 and 7.11% of the S_{max} for the 15, 30 and 55 kg ha⁻¹ treatments, respectively. For the mineral soil, the proportions were 0.98, 1.78 and 3.26% of the S_{max} . When the amount of TP released in leachate is calculated as the percentage of what was applied in the slurry (Table 2), most of the TP applied was retained in the soils, with percentages lower than 2% for the organic soil. For the mineral soil, the values were similar, although a 7.3% recovery was obtained for the 15 split applications.

Although organic soils are considered to have low sorption capacities for P due to competition between phosphate anions and humic/fulvic acids and occlusion of OM for sorption sites (Guppy et al. 2005), the amounts of P obtained in leachate highlight the elevated ability of the organic soil used in this study to retain freshly added P. The disruption of the soil structure when packing the columns, with the breakage of soil aggregates, likely enhanced the ability of

the soil to immobilise soluble P applied in the slurry by the activation of sorption sites that were occluded by the native OM of the soil (Margenot et al. 2017; Muukkonen et al. 2009). Disturbed soil columns may have created new reaction surfaces and, consequently, increased the soils' ability to sorb: the presence of new carbonates (Sø et al. 2011), clay minerals (Gérard 2016) and Al and Fe oxide (Antelo et al. 2007) sorption sites from the breakage of the soil aggregates may have further promoted the P retention capacity. In the case of Al and Fe oxides, this enhanced sorption ability may have been promoted by the formation of tertiary compounds between the metals and organic acids, especially abundant in soils with high OM content (Riddle et al. 2018). Additionally, in organic soils, subsurface flow is the predominant path of P transport due to the tendency to develop macropores and cracks following drying and wetting cycles under natural conditions as a consequence of its hydrophobicity (Simmonds et al. 2017; Litaor et al. 2006). Disturbed organic soils likely destroyed the pore network, and therefore contributed to the observed small mass release of P in the leachate.

3.3 Nitrogen in leachate

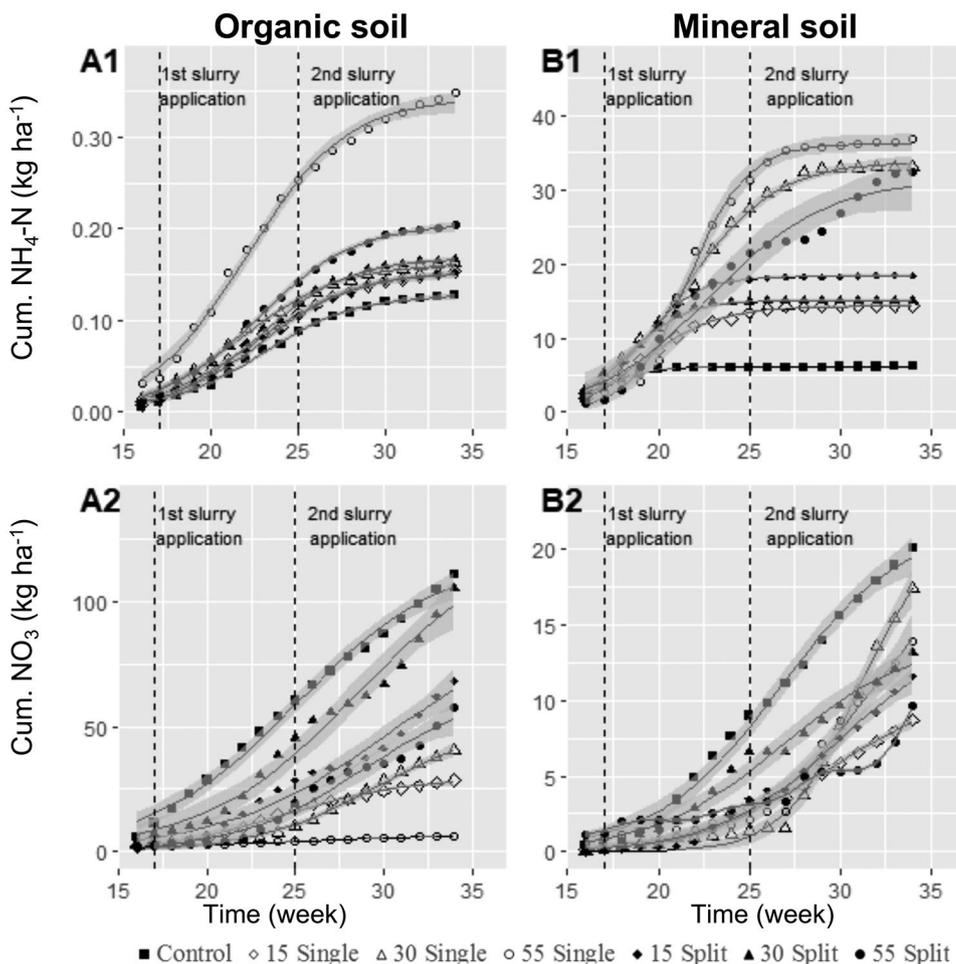
The ANOVA analysis showed no statistical difference ($p > 0.05$) in the NH₄-N loads between the different treatments and the control in the organic soil, except for the single 55 kg ha⁻¹ treatment (Fig. 2—A1). For the mineral soil, single applications of 30 and 55 kg ha⁻¹ and the split application of 55 had a statistically significant effect ($p < 0.001$) on the NH₄-N loads compared to the control (Fig. 2—B1), raising them in all cases. Among soils, NH₄-N loads in the leachate water were significantly higher ($p < 0.001$) in the mineral soil than the organic soil. The NH₄-N in the leachate from the mineral soil ranged from 6 to 36 kg ha⁻¹ compared to the very low values for the organic soil, which ranged from 0.1 to 0.3 kg ha⁻¹. The NH₄-N released in leached water as a percentage of the NH₄-N applied in the slurry was lower than 1% in the organic soil, but ranged from 18 to 54% in the mineral soil (Table 3). Therefore, it is likely that NH₄-N applied in the slurry, which was equivalent to 38% of the TN, was partially held in the cationic sorption soil sites of the organic soil due to its relatively high CEC (32.4 meq/100 g) and subjected to a more intense nitrification process than in the mineral soil (Vymazal 2007). By contrast, the lower CEC of the mineral soil (17 meq/100 g) may have facilitated mobilisation of the positively charged NH₄-N through the columns.

Over the duration of the study, cumulative NO₃-N losses from all treatments were substantially higher from the organic soil columns than from the mineral soil columns, indicating a more efficient nitrification process. In the mineral soil, the nitrification process may have occurred

Table 2 Percentage recovery of TP in leachate, calculated as the difference between the total P leached at each treatment and the control divided by the amount of P applied in the slurry

Slurry application (kg ha ⁻¹)	Soil type	
	Organic	Mineral
Single		
15	1.62	0.930
30	0.430	1.99
55	0.710	0.970
Split		
15	1.55	7.32
30	0.610	0.690
55	0.160	1.06

Fig. 2 Average cumulative leaching of ammonium (NH₄-N) and nitrate (NO₃-N) for each treatment and soil type. Fitted lines represent a 3-parameter logistic model with 95% confidence intervals (CI). Dashed lines indicate slurry application times (week 17 and week 25)



to a lesser extent than in the organic soil, possibly due to the lower C/N ratio as a consequence of the smaller initial amount of OM in the soil compared to the organic soil (Chen et al. 2015; Zhang et al. 2015). For the organic soil, leached losses of NO₃-N were statistically lower in all treatments

than from the control, except for the split 30 kg ha⁻¹ (Fig. 2—A2). Similarly, NO₃-N releases were lower in the amended columns than the control columns, although they were not statistically different (Fig. 2—B2). The higher concentration of NO₃-N in the control columns in both soils may be due to a denitrification process of the native OM of the soils and the organic N in the slurry. Although gaseous N was not measured, denitrification may be the only process explaining the lower NO₃-N loads in amended columns compared to unamended (control) columns. As was the case for the P, split slurry applications did not have a significant impact in the mass released in leachate over the period of study. Only the mineral soil showed an increase in the NH₄-N load for the first application of the split 55 kg ha⁻¹ treatment 4 weeks after it was applied.

Table 3 Percentage recovery of NH₄-N in leachate, calculated as the difference between the total NH₄-N leached in leachate water at each treatment and the control divided by the amount of NH₄-N applied in the slurry

Slurry application (kg ha ⁻¹)	Soil type	
	Organic	Mineral
Single		
15	0.590	32.5
30	0.310	53.7
55	0.370	33.3
Split		
15	0.580	49.1
30	0.320	17.8
55	0.250	28.6

4 Conclusions

This study found that split applications did not produce a significantly lower P release in the leachate when compared with their single counterparts, although this lack of effect

may have been masked by the artificially enhanced ability of the soils used here to retain P. Although $\text{NH}_4\text{-N}$ loads in leachate increased proportionally with the slurry application rate in the mineral soil, the losses for the organic soil were negligible. However, the $\text{NO}_3\text{-N}$ released in leachate from the organic soil was greater than from the mineral soil at all the treatments. Split applications of fertiliser had little effect on N released in leached water, suggesting that these fertiliser management practices may have little impact on N losses in subsurface transportation. This indicates that the amount of fertiliser, as opposed to its application regime, would seem to exert the highest effect in nutrient losses.

Acknowledgements This work was funded by the Irish Department of Agriculture, Forestry and the Marine (project reference 13/S488) as part of the Research Stimulus Fund 2013. The authors would like to thank the landowners for generously providing the soils used in this study and to Dr. John Murnane, D. McDermott, E. Kilcullen and M. B. O'Shea for their valuable advice and support in the use of University of Galway laboratories and facilities.

Declarations

Research involving human participants and/or animals N/A

Informed consent N/A

Competing interests The authors declare no competing interests.

References

- Antelo J, Arce F, Avena M, Fiol S, López R, Macías F (2007) Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma* 138:12–19. <https://doi.org/10.1016/j.geoderma.2006.10.011>
- APHA (2005) Standard methods for the examination of water and wastewater. Am Public Heal Assoc, Washington, DC, USA
- ASTMD (2002) Standard test method for particle-size analysis of soils (D422). West Conshohocken, PA, Philadelphia, PA
- Beauchemin S, Simard RR (1999) Soil phosphorus saturation degree: Review of some indices and their suitability for P management in Québec, Canada. *Can J Soil Sci* 79:615–625. <https://doi.org/10.4141/S98-087>
- Brennan RB, Fenton O, Grant J, Healy MG (2011) Impact of chemical amendment of dairy cattle slurry on phosphorus, suspended sediment and metal loss to runoff from a grassland soil. *Sci Tot Environ* 409:5111–5118. <https://doi.org/10.1016/j.scitotenv.2011.08.016>
- Brennan RB, Wall DP, Fenton O, Grant J, Sharpley AN, Healy MG (2014) Impact of chemical amendment of dairy cattle slurry on soil phosphorus dynamics following application to five soils. *Commun Soil Sci Plant Anal* 45:2215–2233. <https://doi.org/10.1080/00103624.2014.912293>
- BS 1377-2 (1990) Methods of test for soils for civil engineering purposes British Standards Institution London
- Chen Z, Ding W, Xu Y, Müller C, Rütting T, Yu H, Fan J, Zhang J, Zhu T (2015) Importance of heterotrophic nitrification and dissimilatory nitrate reduction to ammonium in a cropland soil: Evidences from a ^{15}N tracing study to literature synthesis. *Soil Biol Biochem* 91:65–75. <https://doi.org/10.1016/j.soilbio.2015.08.026>
- Constantin J, Mary B, Laurent F, Aubrion G, Fontaine A, Kerveillant P, Beaudoin N (2010) Effects of catch crops, no till and reduced nitrogen fertilisation on nitrogen leaching and balance in three long-term experiments. *Agric Ecosyst and Environ* 135:268–278. <https://doi.org/10.1016/j.agee.2009.10.005>
- Creamer R, Simo I, Reidy B, Carvalho J, Fealy R, Hallet S, Jones R, Holden A, Holden N, Hannam J, Massey P, Mayr T, McDonalds E, O'Rourke S, Sills P, Truckell I, Zawadzka J, Schulte R (2014) Irish Soil Information System: integrated synthesis report. Environmental Protection Agency, Johnstown Castle, Wexford, Ireland
- Davis CS (2002) Statistical methods for the analysis of repeated measurements. Springer texts in statistics. Springer, New York
- Gérard F (2016) Clay minerals, iron/aluminum oxides, and their contribution to phosphate sorption in soils — a myth revisited. *Geoderma* 262:213–226. <https://doi.org/10.1016/j.geoderma.2015.08.036>
- Gerke J (2010) Humic (organic matter)-Al(Fe)-phosphate complexes. *Soil Sci* 175:417–425. <https://doi.org/10.1097/SS.0b013e3181fb4dd>
- González Jiménez JL, Daly K, Roberts WM, Healy MG (2019) Split phosphorus applications as a strategy to reduce incidental phosphorus losses in surface runoff. *J Environ Manag* 242:114–120. <https://doi.org/10.1016/j.jenvman.2019.04.046>
- Guérin J, Parent L-É, Abdelhafid R (2007) Agri-environmental thresholds using Mehlich III soil phosphorus saturation index for vegetables in histosols. *J Environ Qual* 36:975–982. <https://doi.org/10.2134/jeq2006.0424>
- Guppy CN, Menzies NW, Moody PW, Blamey FPC (2005) Competitive sorption reactions between phosphorus and organic matter in soil: a review. *Aust J Soil Res* 43:189–202. <https://doi.org/10.1071/SR04049>
- Hart MR, Quin BF, Nguyen ML (2004) Phosphorus runoff from agricultural land and direct fertilizer effects. *J Environ Qual*. <https://doi.org/10.2134/jeq2004.1954>
- Hou L, Hu BX, Qi Z, Yang H (2018) Evaluating equilibrium and non-equilibrium transport of ammonium in a loam soil column. *Hydrol Stud* 32:80–92
- IUSS Working Group WRB (2014) World reference base for soil resources 2014. World Soil Resour Reports 106:1–191
- Keresztesi Á, Nita I-A, Birsan M-V, Bodor Z, Pernyeszi T, Micheu MM, Szép R (2020) Assessing the variations in the chemical composition of rainwater and air masses using the zonal and meridional index. *Atmos Res* 237:104846. <https://doi.org/10.1016/j.atmosres.2020.104846>
- Kovar JL, Pierzynski GM (2009) Methods of phosphorus analysis for soils, sediments, residuals, and waters. Southern Cooperative Series Bulletin No. 408
- Litaor MI, Eshel G, Reichmann O, Shenker M (2006) Hydrological control of phosphorus mobility in altered wetland soils. *Soil Sci Soc Am J* 70:1975–1982. <https://doi.org/10.2136/sssaj2005.0316>
- Macintosh KA, Mayer BK, McDowell RW, Powers SM, Baker LA, Boyer TH, Rittmann BE (2018) Managing diffuse phosphorus at the source versus at the sink. *Environ Sci and Technol* 52:11995–12009. <https://doi.org/10.1021/acs.est.8b01143>
- Mallarino AP, Sawyer JE, Barnhart SK (2013) A general guide for crop nutrient and limestone recommendations in Iowa. Iowa State University. <https://www.agronext.iastate.edu/soilfertility/info/PM1688.pdf>. Accessed 4 July 2022
- Marginot AJ, Paul BK, Sommer RR, Pulleman MM, Parikh SJ, Jackson LE, Fonte SJ (2017) Can conservation agriculture improve phosphorus (P) availability in weathered soils? Effects of tillage and residue management on soil P status after 9 years in a Kenyan Oxisol. *Soil Till Res* 166:157–166. <https://doi.org/10.1016/j.still.2016.09.003>
- Mazloomi F, Jalali M (2019) Effects of vermiculite, nanoclay and zeolite on ammonium transport through saturated sandy loam soil: Column

- experiments and modeling approaches. *CATENA* 176:170–180. <https://doi.org/10.1016/j.catena.2019.01.014>
- McGeehan SL, Naylor DV (1988) Automated instrumental analysis of carbon and nitrogen in plant and soil samples. *Commun Soil Sci Plant Anal* 19:493–505. <https://doi.org/10.1080/00103628809367953>
- Mclean EO (1982) Soil pH and lime requirement, in: *Methods of soil analysis. Part 2. Chemical and microbiological properties*, Agronomy Monograph SV - 9.2. American Society of Agronomy, Soil Science Society of America, Madison, WI, pp 199–224. <https://doi.org/10.2134/agronmonogr9.2.2ed.c12>
- Mehlich A (1984) Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. *Commun Soil Sci Plant Anal* 15:1409–1416. <https://doi.org/10.1080/00103628409367568>
- Miri S, Davoodi SM, Robert T, Brar SK, Martel R, Rouissi T (2022) Enzymatic biodegradation of highly p-xylene contaminated soil using cold-active enzymes: a soil column study. *J Haz Mat* 423:127099
- Morgan MF (1941) Chemical soil diagnosis by the universal soil testing system. *CT Agric Exp Stn Bull*
- Murnane JG, Fenton O, Healy MG (2018) Impacts of zeolite, alum and polyaluminum chloride amendments mixed with agricultural wastes on soil column leachate, and CO₂ and CH₄ emissions. *J Environ Manage* 206:398–408. <https://doi.org/10.1016/j.jenvman.2017.10.046>
- Muukkonen P, Hartikainen H, Alakukku L (2009) Effect of soil structure disturbance on erosion and phosphorus losses from Finnish clay soil. *Soil Tillage Res* 103:84–91. <https://doi.org/10.1016/j.still.2008.09.007>
- Parvage MM, Ulén B, Kirchmann H (2015) Nutrient leaching from manure-amended topsoils (Cambisols and Histosols) in Sweden. *Geoderma Reg* 5:209–214. <https://doi.org/10.1016/j.geodrs.2015.08.003>
- Riddle M, Bergström L, Schmieder F, Kirchmann H, Condrón L, Aronsson H (2018) Phosphorus leaching from an organic and a mineral arable soil in a rainfall simulation study. *J Environ Qual* 47:487–495. <https://doi.org/10.2134/jeq2018.01.0037>
- Roberts WM, Gonzalez-Jimenez JL, Doody DG, Jordan P, Daly K, Gan J (2017) Assessing the risk of phosphorus transfer to high ecological status rivers: integration of nutrient management with soil geochemical and hydrological conditions. *Sci Tot Environ* 589:25–35. <https://doi.org/10.1016/j.scitotenv.2017.02.201>
- Ross D (1995) Recommended soil tests for determining exchange capacity. In: Sims JT, Wolf A (eds) *Recommended soil testing procedures for the northeastern United States*. Ag Experiment Station, University of Delaware, Newark, Delaware
- Roy AC, De Datta SK (1985) Phosphate sorption isotherms for evaluating phosphorus requirement of wetland rice soils. *Plant Soil* 86:185–196. <https://doi.org/10.1007/BF02182893>
- Schulte EE, Hopkins BG (1996) Estimation of soil organic matter by weight loss-on-ignition. In: *Soil organic matter: analysis and interpretation*, SSSA Special Publication SV - 46. Soil Science Society of America, Madison, WI, pp 21–31. <https://doi.org/10.2136/sssaspecpub46.c3>
- Simmonds B, McDowell RW, Condrón LM (2017) The effect of soil moisture extremes on the pathways and forms of phosphorus lost in runoff from two contrasting soil types. *Soil Res* 55:19–27
- Sø HU, Postma D, Jakobsen R, Larsen F (2011) Sorption of phosphate onto calcite; results from batch experiments and surface complexation modeling. *Geochim Cosmochim Acta* 75:2911–2923. <https://doi.org/10.1016/j.gca.2011.02.031>
- Sommers LE, Nelson DW (1972) Determination of total phosphorus in soils: a rapid perchloric acid digestion procedure. *Soil Sci Soc Am J* 36:902–904. <https://doi.org/10.2136/sssaj1972.03615995003600060020x>
- Vymazal J (2007) Removal of nutrients in various types of constructed wetlands. *Sci Tot Environ* 380:48–65. <https://doi.org/10.1016/j.scitotenv.2006.09.014>
- Walsh S (2012) A summary of climate averages for Ireland 1981–2010. Met Eireann, Dublin
- Wall DP, Plunkett M (2020) Major and minor micronutrient advice for productive agricultural crops. Dublin. <https://www.teagasc.ie/media/website/publications/2020/Major--Micro-Nutrient-Advice-for-Productive-Agricultural-Crops-2020.pdf>
- Wang W, Wu X, Yin C, Xie X (2019) Nutrition loss through surface runoff from slope lands and its implications for agricultural management. *Agric Wat Manage* 212:226–231. <https://doi.org/10.1016/j.agwat.2018.09.007>
- Zhang J, Wang J, Zhong W, Cai Z (2015) Organic nitrogen stimulates the heterotrophic nitrification rate in an acidic forest soil. *Soil Biol Biochem* 80:293–295. <https://doi.org/10.1016/j.soilbio.2014.10.024>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.