



Effects of fertiliser on phosphorus pools in soils with contrasting organic matter content: A fractionation and path analysis study



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ABSTRACT

With the intensification of agricultural production in many European countries, more marginal soils with elevated organic matter (OM) content are being brought into cultivation. However, little is known about the transformations in the constituent phosphorus (P) pools of organic soils receiving applications of P fertiliser. Soil P fractions were measured before and after receiving fertiliser in a controlled experiment to determine the change in the soil pools and path analysis was used to evaluate the relationships between P pools. In this study, P deficient soils ranging in OM content from 8 to 76%, were placed in large pots, planted with ryegrass and subjected to P fertiliser applications ranging from 10 to 145 kg ha⁻¹, and monitored over an eight-month study period. High OM soils had a diminished ability to build-up the labile pool from freshly applied P, with relatively low increases up to 200% of the initial value, compared to mineral soils in which the labile pool increased to > 2500% of the initial concentration. Additionally, organic soils had higher P uptakes in the grass yield than mineral soils, indicating a higher availability of added P in the soil solution than mineral soils due to their limited sorption ability. In general, there was a reduction in the organic P pool over applications from 0 to 55 kg ha⁻¹, which was indicative of partial mineralization, but was followed by an accumulation of added P over applications from 55 to 145 kg P ha⁻¹. The residual P pools did not build-up with P additions, but data indicated the occurrence of mineralization in most of the soils with decreases of around 40% of the initial concentrations. Organic and residual pools therefore displayed potential to supply P to more labile P pools across all soils of this study. Path analysis indicated that applied P was the only source of labile P in the soil with the highest OM content, leaving it dependent on continuous P applications to supply P for productivity, whereas in the rest of the soils there were interrelations between the non-labile and labile pools. Low pH strongly immobilised the applied P and should be corrected before the initiation of any fertilisation program, even in soils deficient in plant available P. The results demonstrated that P added as fertiliser to organic soils does not accumulate as in mineral soils, which may leave them susceptible to P losses in surface runoff. Therefore, organic soils under agricultural production located in high status catchments should receive low P applications and only during periods with low probability of precipitation to minimise the possibility of P exports to receiving waters.

1. Introduction

The maintenance of grasslands for livestock production often requires the application of nutrients in the form of fertilisers to balance the exports derived from that productivity. Among the nutrients incorporated, phosphorus (P) is of special consideration because of its essential contribution to plant growth, but also for its complex chemistry within the soil matrix (Epstein and Bloom, 2004; Pierzynski and McDowell, 2005). When applied in excess of the crop requirements, P accumulates in soil which may increase the risk of P losses to water bodies leading to eutrophication (Carpenter, 2008).

Histosols and other peat-derived soil, often described as organic soils (Creamer et al., 2014), typically contain large amounts of organic matter (OM) at the surface and have poor P retention capacities (Guppy et al., 2005; Daly et al., 2001). With a total land area of approximately 7% in Europe (Montanarella et al., 2006), organic soils have received relatively little attention regarding P management. In the Republic of Ireland, approximately 840,000 ha of organic soils are currently or potentially under agricultural production (Renou-Wilson et al., 2011). Many of these soils are located in upland, remote areas and set within high ecological status or pristine water bodies identified under the European Water Framework Directive (OJEC, 2000). This regulation

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Table 1

Selected physico-chemical properties of the six soils used in the study. Values in parenthesis represent standard deviations, except for the fractions Fe-Al bound P, Organic P and Residual P, which are standard errors of the mean.

Soil property	Units	Galway peat	Galway peaty mineral	Cork mineral	Cork peaty mineral	Wexford mineral	Wexford peaty mineral
Classification ^a		Ombic Histosol	Haplic Cambisol	Haplic Stagnosol	Haplic Stagnosol	Haplic Cambisol	Haplic Podzol
Texture		Sandy loam	Sandy loam	Clay loam	Sandy clay loam	Loam	Sandy loam
Clay	g kg ⁻¹	42	98	297	71	182	101
Silt	g kg ⁻¹	20	184	345	58	365	186
Sand	g kg ⁻¹	174	360	266	203	366	572
Organic matter	g kg ⁻¹	764	358	91	668	87	141
pH		5.3	6.6	5.1	4.5	6.0	6.2
Dry bulk density	g cm ⁻³	0.2	0.6	0.6	0.2	1.2	0.7
Total C	g kg ⁻¹	403.0	177.0	42.0	347.0	30.9	70.0
Organic C	g kg ⁻¹	387.4	152.6	39.5	341.9	26.2	65.3
Total N	g kg ⁻¹	16.3	14.2	3.6	22.0	3.0	4.4
Mehlich-3	mg kg ⁻¹						
Al		2.6 (0.4)	61.5 (9.8)	884.9 (13.9)	605.0 (25.5)	947.0 (2.6)	991.4 (46.4)
Fe		222.1 (18.1)	238.5 (6.0)	262.4 (4.0)	507.4 (15.2)	117.0 (2.0)	256.4 (10.1)
Ca		7812.6 (175.5)	8216.0 (126.5)	656.1 (2.7)	2414.0(19.4)	1103.1 (3.8)	2105.6 (39.3)
P		13.7 (0.7)	6.5 (0.0)	20.6 (0.2)	31.1 (1.1)	23.3 (0.2)	25.6 (0.6)
Labile P	mg kg ⁻¹	33.5 (0.1)	4.2 (0.4)	2.0 (0.2)	38.4 (2.7)	3.0 (0.7)	1.4 (0.2)
Fe-Al bound P	mg kg ⁻¹	47.4 (1.0)	111.0 (8.6)	20.4 (0.8)	103.1 (3.1)	194.1 (4.2)	37.0 (0.8)
Organic P	mg kg ⁻¹	146.4 (0.3)	350.7 (5.3)	186.2 (1.2)	535.3 (5.0)	332.5 (6.1)	307.5 (2.2)
Ca bound P	mg kg ⁻¹	43.5 (3.0)	287.5 (91.6)	12.3 (1.8)	47.9 (3.5)	127.9 (7.4)	118.7 (8.7)
Residual P	mg kg ⁻¹	335.1 (2.4)	369.9 (23.8)	148.3 (0.9)	376.9 (7.8)	516.9 (2.7)	158.1 (2.7)
Total P	mg kg ⁻¹	605.8 (8.5)	1116.7 (10.5)	369.1 (2.6)	1101.5 (29.1)	1174.2 (0.9)	622.6 (5.6)

^a World Reference Base 2014 (IUSS Working Group WRB, 2014).

encourages member states to maintain “high” ecological water status where it exists and to achieve at least “good” ecological status for all water bodies. However, with the intensification of agricultural practices across Europe, these sites often receive high P inputs similar to those usually applied in areas under intensive livestock production (Roberts et al., 2017), and recent studies have linked the loss of “high ecological status” in these catchments to these practices (White et al., 2014). Therefore, it is essential to understand the impact of fertiliser applications on the P chemistry in organic soils and to evaluate possible negative effects of P management, if the quality of the sensitive catchments to agricultural practices is to be maintained.

Phosphorus applied to soils undergoes a series of physico-chemical (dissolution-precipitation and desorption-adsorption) transformations regulated by soil characteristics such as mineralogy composition, surface area, pH, extractable iron-aluminium (Fe-Al) hydroxides and OM content (Guérin et al., 2011; Janardhanan and Daroub, 2010; Frossard et al., 2000; Porter and Sanchez, 1992). Phosphorus fertiliser recommendations on mineral soils are based on their ability to sorb and gradually build-up P over time until a critical level is reached, followed by the maintenance of that level by replacing the P removed by consecutive harvests (Voss, 1998; Olson et al., 1987). However, the ability of organic soils to sorb and retain P applied is impeded by the inherent large amounts of OM that compete for sorption sites (Guppy et al., 2005; Daly et al., 2001), so that the approach of build-up of P and maintenance on these soils for fertiliser recommendations has been questioned (Roberts et al., 2017; Daly et al., 2015).

The sequential P fractionation procedure, developed by Hedley et al. (1982), extracts P bound from diverse inorganic and organic compounds of different lability using solutions of increasing extracting strength (Cross and Schlesinger, 1995). Despite its limitations when providing P speciation at the P fraction level and the likelihood to overestimate organic P (Turner et al., 2005), the Hedley method is one of the most comprehensive methodologies used to evaluate the soil P cycle and dynamics into “operationally-defined fractions” of different availability and nature (Condon and Newman, 2011; Negassa and Leinweber, 2009). However, only a few studies have applied this technique in OM-rich soils (Schlichting et al., 2002; Cross and Schlesinger, 1995) and, to our knowledge, none exists in organic soils where the effect of P applied in the different soil P pools has been evaluated using this technique. Therefore, there is a lack of knowledge

about the interaction of freshly applied P with the different soil P fractions when organic acids are in direct competition for the same reaction sites as the P applied. Phosphorus assimilation and turnover in agricultural organics soils is poorly understood and needs further research in order to improve their management and minimise potential P losses to the environment.

Sequential P fractionation techniques alone do not provide insight on the relationships and transformations between the soil P pools under different treatments, nor behavioural comparison of soils of different pedogenesis receiving the same treatments (Gama-Rodrigues et al., 2014; Zheng et al., 2004). Path analysis has been shown to be a valuable tool to evaluate the cause-and-effect interrelations between P pools in different soil types and under a variety of management regimes (Tiecher et al., 2018; Zheng et al., 2004; Beck and Sanchez, 1994; Tiessen et al., 1984).

Therefore, the objectives of this study were (1) to assess the changes in the different soil P fractions receiving increasing amounts of P fertiliser, and (2) to examine which pools acted as sinks or sources for P so as to gain a better understanding of the soil P cycle. To address these objectives, six soils deficient in available P and ranging in OM content were placed in large pots and received fourteen increasing amounts of P fertiliser under ryegrass growth, and were subjected to P fractionation and path analyses.

2. Materials and methods

2.1. Pot experiment

Six grassland soils deficient in P and representing a range of OM content, were selected from three high status catchments in the Republic of Ireland (Table 1). All soils were under a low intensity grazing system and received no P applications in the years prior to soil collection, with the exception of Galway peaty mineral, which received P applications of approximately 32 kg P ha⁻¹y⁻¹ in the years prior to the soil collection. The soils were collected from the surface horizon (0–20 cm), air dried, and sieved through a 12 mm mesh. A subsample was taken from each soil and analysed for selected physico-chemical properties and to determine initial P concentrations in the different P pools defined below (Table 1).

Soils were rewetted to their field gravimetric water content and

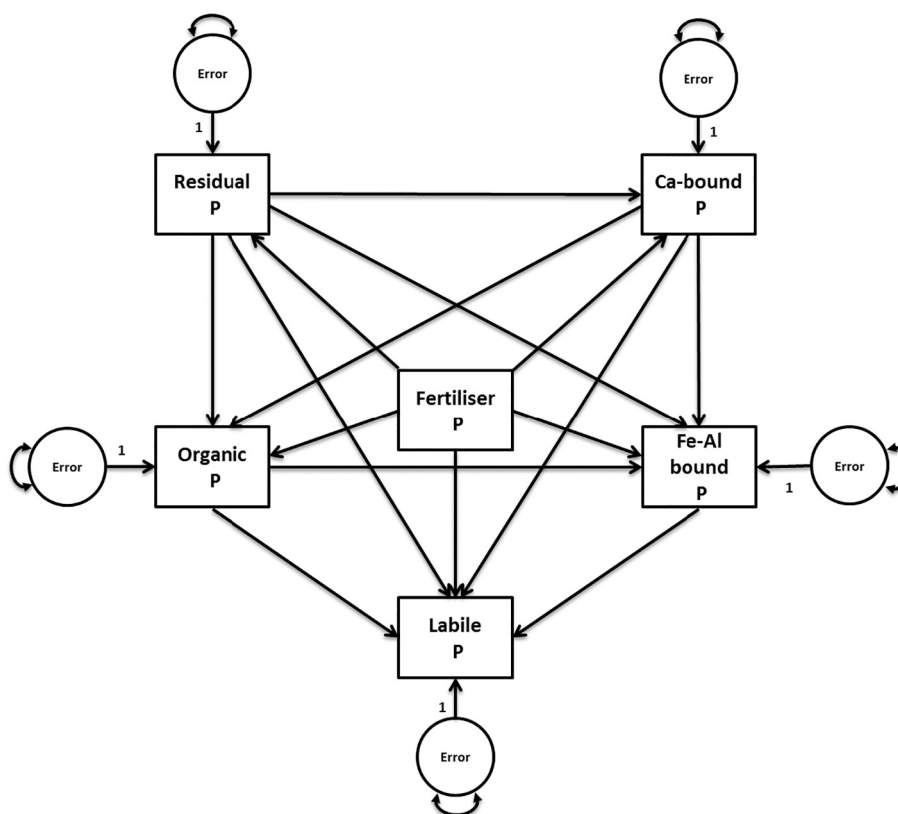


Fig. 1. Path diagram with the proposed relationships between the different soil P pools and P fertiliser applications. Errors represent the variance of each of the dependent variables (five soil P pools).

placed in 18.5 L pots (0.3 m upper diameter, 0.3 deep). Each soil received fourteen P fertiliser applications ($n = 2$) as single superphosphate (16% P content) at rates equivalent to 0, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 70, 100 and 145 kg P ha^{-1} . Each pot received an initial application of nitrogen (N) as calcium ammonium nitrate and potassium (K) as potassium chloride, at a rate equivalent to 55 kg ha^{-1} and 245 kg ha^{-1} , respectively. Pots were sown with perennial ryegrass (*Lolium perenne* L.) seeds at a rate equivalent to 28 g m^{-2} and placed in a glasshouse for three months under the following conditions: average temperature of 11.1°C ($\pm 3.9^\circ\text{C}$) and relative humidity of 82% ($\pm 12\%$). Pots were then placed in controlled growth chambers operated in the following conditions: (1) photoperiod of 16 h light (2) daytime temperatures of 14°C and night-time temperatures of 8°C , with respectively relative humidities of 85% and 75%, and (3) photosynthetically active radiation of $450 \pm 50 \mu\text{mol m}^{-2} \text{ s}^{-1}$. The pots were randomly placed in the chambers and were held between 60 and 90% field capacity by weighting them regularly. The grass was harvested six times when it attained a length of 22–26 cm. At the end of the experiment, and for each pot, six soil cores were taken, oven-dried at 40°C for three days, composited and subjected to soil P fractionation analysis. Phosphorus use efficiency and magnitude of grass response to P fertilisations in these soils were evaluated, the details of which are in González Jiménez et al. (in press).

2.2. Soil P fractionation

A modified Hedley fractionation procedure (Hedley et al., 1982) was used for each soil and P treatment to determine the different fractions before and after the experiment. The iron-oxide paper strip method (Menon et al., 1989) was used as an alternative to the traditionally used but laborious resin-P method (Chardon et al., 1996). Additionally, the iron-oxide paper strip test is more suitable for soils of different nature as its ability to determine dissolved and loosely bound

P is not influenced by physical or chemical properties of the soils (Robinson and Sharpley, 1994). Duplicate 0.5 g samples of dried soil were weighed in 50 ml polypropylene tubes and shaken in 40 ml of 0.01 M CaCl_2 with iron-oxide paper strips for 16 h using a reciprocal shaker operated at 6 rpm. Phosphorus adsorbed to the iron strips was dissolved by shaking the strips for 1 h in 40 ml 0.1 M H_2SO_4 . This fraction was identified as the FeO strip-P. The soil suspension was then centrifuged at approximately $51,845 \text{ m s}^{-1}$ for 20 min and the supernatant was decanted. The soil was then sequentially extracted with: (1) 30 ml of 0.5 M NaHCO_3 at pH 8.5 ($\text{NaHCO}_3\text{-P}$) (2) 0.1 M NaOH (NaOH-P), and (3) 1 M H_2SO_4 ($\text{H}_2\text{SO}_4\text{-P}$), each of them at the same shaking and centrifuging settings as described for the FeO strip-P. The residual P fraction resisting the 1 M H_2SO_4 extraction was calculated as the difference between total P (P_t) and the sum of FeO strip-P + $\text{NaHCO}_3\text{-P}$ + NaOH-P + $\text{H}_2\text{SO}_4\text{-P}$. Total P was determined by ICP-OES in a separate 0.5 g dried sample using the microwave-assisted acid digestion method (USEPA, 1996). Inorganic P (P_i) concentrations for all the extractants were determined within 24 h using the ascorbic acid-molybdenum blue method (Kuo, 1996). The P_t concentration in the different extractants (except for the FeO strip-P, where only P_i was determined) was determined by acid potassium persulfate digestion. Organic P concentrations (P_o) in the NaHCO_3 and NaOH fractions were calculated as the difference between P_t and P_i .

The different chemically extracted fractions were grouped into operationally defined pools of increasing recalcitrance as follows: (1) the FeO strip-P represented the labile P pool and comprised P dissolved in the soil solution along with loosely adsorbed P (2) the $\text{NaHCO}_3\text{-P}_i$ and NaOH-P_i represented the Fe-Al bound P pool and included moderately sorbed and/or fixed P_i by Al and Fe oxides/hydroxides (3) analogous to the Fe-Al bound P, the $\text{NaHCO}_3\text{-P}_o$ + NaOH-P_o represented the organic P pool (4) the $\text{H}_2\text{SO}_4\text{-P}$ represented the Ca-bound P pool and comprised stable P contained in primary minerals such as apatite (5) the residual P pool, calculated as the difference between the P_t and the sum of the

previous pools, comprised highly stable organometallic complexes and organic materials such as lignin (Gama-Rodrigues et al., 2014; Condon and Newman, 2011; Negassa and Leinweber, 2009; Schlichting et al., 2002; Cross and Schlesinger, 1995).

2.3. Statistical analysis

In order to analyse and evaluate the impact of the increasing P fertiliser applications on the different soil P pools, the percentage change for each soil and P pool were calculated as the difference between the P concentration after and before the experiment divided by the original P concentration. Path analysis was used to examine the cause-and-effect relationships between the soil P pools and P fertiliser, and to differentiate between the direct and indirect effects of these relationships. Phosphorus concentrations (in mg kg^{-1}) at each P application dose (kg ha^{-1}) for each soil pool the end of the experiment were used in the path analysis. The conceptual diagram in Fig. 1 was proposed as a general model to test P transformations and dynamics in the different soils. Phosphorus fertiliser was the sole independent variable that may affect the different soil P pools. Therefore, the soil P pools were considered as dependent variables. A basic assumption of the model is that, under cultivation conditions where soils are mainly aerated most time of the year, P movements between the soil P pools occur from the most recalcitrant pools to the less recalcitrant ones and not vice-versa, as might happen under flooded conditions where the redox conditions would change (Castillo and Wright, 2008). This is represented in the model by the different arrows between the independent variable and the dependent variables, and within the dependent variables following the assumption mentioned above (Fig. 1). Each potential relationship in the model (cause) is measured by a partial regression coefficient (direct effect). They are analogous to the covariance between two variables and are referred to as path coefficients (β). Indirect effects are referred to as the effects between two variables that are mediated by another intervening variable (Raykov and Marcoulides, 2006). Both unstandardized (raw score units) and standardized (standard deviation units) path coefficients were calculated. The use of unstandardized path coefficients enabled comparison for the same variable relationship across the different soils, whereas standardized path coefficients were better for comparing different variable relationships within the same soil (Beaujean, 2014).

The generic model represented in Fig. 1 is a saturated model with zero degrees of freedom, that is, there are as many estimated parameters as data points (observations). By definition, saturated models exhibit perfect fit to the data and hence they cannot be confirmed or invalidated by the path analysis (Raykov and Marcoulides, 2006). However, this model was used as a benchmark against which nested (modified) models with positive degrees of freedom could be tested. Modifications of the saturated model were done by dropping from the model the non-significant path coefficients stepwise until final models were tenable, analogous to backward selection in regression analysis, so that the likelihood to miss a plausible variable was excluded. The Chi square test (χ^2), at a significance level of 0.05, was used to validate the nested model from the preceding one until the most restrictive, yet plausible, model was achieved for each soil (Raykov and Marcoulides, 2006). Comparative Fit Index (CFI), Expected Cross Validation Index (ECVI), Akaike's Information Criterion (AIC), and Goodness of Fit Index (GFI) were also considered to evaluate the fit strength of the models generated. Analyses were carried out in R statistical software, version 3.4.2 (R Core Team, 2017) using the "lavaan" and "semPlot" packages (Epskamp, 2017; Rosseel, 2012).

3. Results and discussion

3.1. Soils characterization

The physico-chemical characteristics of the soils before the

application of fertiliser are shown in Table 1. The range of OM content reflects a broad variation, spanning from 8.7 to 76.4%, representing the contrasting soil types in high status catchments in Ireland (White et al., 2014). Soil pH was acidic for Cork peaty mineral, Cork mineral and Galway peat, with values of 4.5, 5.1 and 5.3, respectively, in contrast with near-to-neutral values for the other soils. Total P in the soils ranged between 369.1 and 1174.2 mg kg^{-1} . From a pedogenic point of view, Galway peat, classified as Ombric Histosol, had similar values to those reported by Yang and Post (2011), but less than other semi-natural or cultivated Histosols reported elsewhere (Schlichting et al., 2002). The other soils in this study had considerably larger P_t concentrations compared to those in the Yang and Post (2011) pedogenic study. There was a significant positive correlation ($r^2 = 0.7$, $p < 0.05$) between soil pH and Ca-bound P fraction, indicating that pH favoured retention of P in this stable fraction from past P additions (Castillo and Wright, 2008; Schlichting et al., 2002). There were no other significant correlations between the remaining fractions and other soil properties. Organic P and residual P were by far the predominant fractions in all the soils, with values ranging from 24.2 to 50.4% and from 25.4 to 55.3% of the P_t , respectively, whereas labile P was the smallest fraction and did not exceed 5.5% of the P_t in any soil (Table 1).

3.2. Changes in P pools over the study duration

Fig. 2 shows the percentage change before and after the pot study in labile P, Fe-Al-bound P, Ca-bound P, organic P and residual P pools in each soil over all P applications. The labile P fraction (Fig. 2a) increased with increasing rates of P applications in all the soils, as expected. Part of the P applied in the form of fertiliser was taken up by the grass, while the rest reacted with the soil matrix and was adsorbed to soil particles. There were negative changes in labile P in Galway peat, Cork peaty mineral and, to a lesser extent, Galway peaty mineral and Wexford mineral, until P applications exceeded threshold values of approximately 45, 35, 25 and 10 kg ha^{-1} , respectively, indicating a partial depletion of the original pool by grass growth and uptake. Here, grass growth may have been impeded due to lack of available P, until the rates of application were enough to support plant growth and replenish the labile P pool. Galway peat and Cork peaty mineral, the soils with the most OM content (Table 1), had relatively low maximum positive percentages of change (around 200%), whereas more mineral soils, such as Wexford peaty mineral and Cork mineral, had maximum positive percentage changes exceeding 2500%. The magnitude at which the labile P pool changed across the P applications is an indication of the ability of each soil to sorb and retain freshly applied P into this fraction. Therefore, high percentage change values mean that large amounts of added P ended up in this pool, whereas low values indicate that only a small amount was tied up here. Phosphorus concentration in the soil solution phase immediately after fertiliser applications is typically very high (saturated solution), and undergoes rapid adsorption reactions on the surface of the soil particles until equilibrium is reached, thus decreasing its concentration to levels typically very small compared to the solid phases (McLaughlin et al., 2011). Mineral soils demonstrated a high ability to adsorb P in the surface areas of their mineral fraction, whereas this adsorption capacity in organic soils was much smaller (Fig. 2a).

Phosphorus not retained in the labile pool of the organic soils was taken up by the plant roots in higher proportions than in mineral soils, as P was readily available in the soil solution and not loosely bound to soil mineral particles. This was evidenced by the higher P uptakes of the organic soils compared to mineral soils (Fig. 3). At high P doses, when it is likely that P has been applied in excess of crop requirements, organic soils with a low % change in labile P showed higher P uptake by the plant roots compared to mineral soils with higher % changes but lower P uptake (Fig. 3). The fertiliser and agronomic responses of this trial are detailed in González Jiménez et al. (in press). Organic soils have low sorption and retention capacities for P (Guppy et al., 2005; Daly et al.,

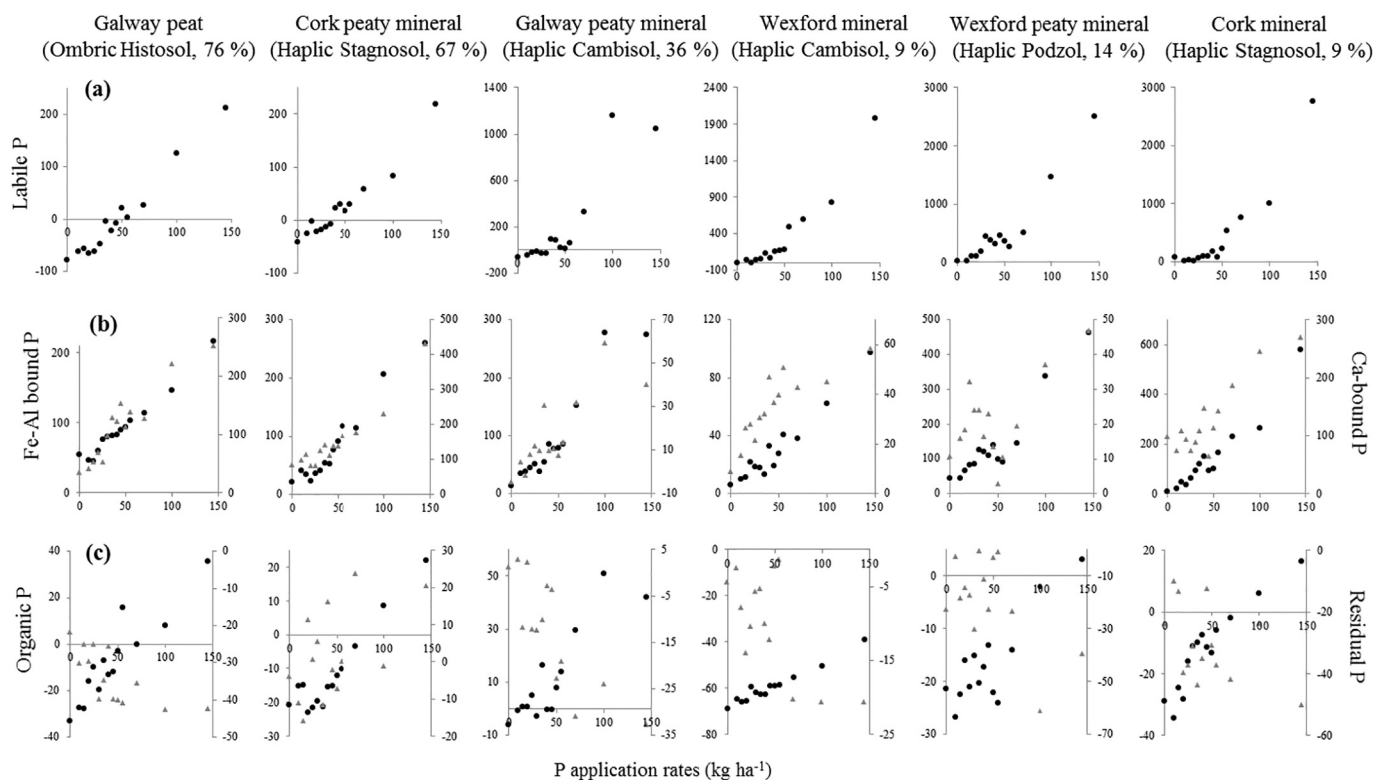


Fig. 2. Percentage change in (a) labile P fraction, (b) Fe-Al bound P (left vertical axis, ● symbol) and Ca-bound P (right vertical axis, ▲ symbol) fractions, and (c) Organic P (left vertical axis, ● symbol) and Residual P (right vertical axis, ▲ symbol) fractions across P applications in the six soils studied. Percentages represent the organic matter content.

2001), so the relative inability of these soils to retain P applied in excess of crop requirements increases the risk of P loss to the aquatic environment (Roberts et al., 2017; Daly et al., 2001). The iron-oxide paper strip method, used as a proxy for the labile P pool, may also have acted as a sink for some dissolved organic P (Robinson and Sharpley, 1994). Although inositol hexaphosphate is the predominant molecule among the organic P compounds, it is relatively resistant to mineralization. However, it is likely that other more degradable molecules, such as phospholipids and nucleic acids, are more abundant in organic soils and therefore prone to be mineralized in the extraction phase with H₂SO₄, overestimating labile P (Quiquampoix and Mousain, 2005; Ivanoff et al., 1998). To minimise this potential source of error and improve the

interpretation of labile P pools, diffusive gradients in thin films (Zhang et al., 2014; Ding et al., 2010) could be used in future studies to efficiently estimate bioavailable P, especially in organic soils where degradable organic P is likely to be present in a higher proportion compared to mineral soils.

The Fe-Al bound and Ca-bound P fractions increased proportionally to the P applications in all the soils (Fig. 2b). There was no clear pattern of P accumulation across the different soils for both P pools, although higher maximum percentage changes (up to 600%) were measured in the Fe-Al bound P in the mineral soils (Cork mineral and Wexford peaty mineral). The short duration of this study likely hindered a better observation of any potential trend between organic and mineral soils.

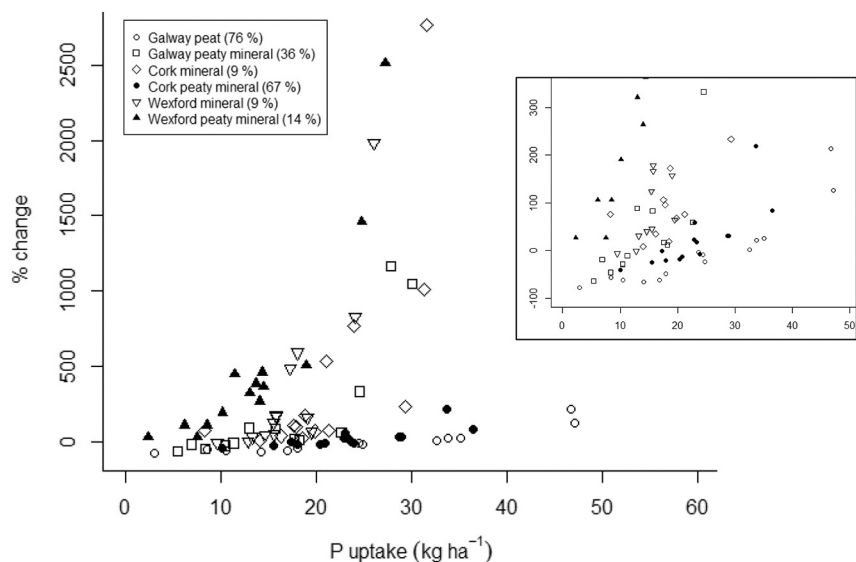


Fig. 3. Relationship between % change in labile P and P uptake for the six soils at each of the 14 fertiliser applications examined in this study. P Uptake was calculated by multiplying the cumulative grass dry matter yield at each P dose by the average herbage P content. The miniature graph represents % change up to 350 in the y-axis to facilitate reading data in that area. Values in parenthesis in the legend represent organic matter content.

None of the soils had negative percentage changes, indicating that there was no depletion of these pools at low P doses during the experiment. With the exception of Cork peaty mineral, the magnitude of change in the Ca-bound P fraction was smaller than the Fe-Al bound P, supporting the hypothesis that this pool is considered a more stable fraction to short-term changes and least reactive to freshly applied P (Cross and Schlesinger, 1995). With no P applied (zero P rate), the percentage of change in these two fractions was positive at the end of the experiment, indicating that P was released from other pools and retained in these fractions. Likely, part of the P contained in the organic P and residual P fractions was mineralized and transferred to these pools.

There was a build-up in the organic P pool across the P treatments (Fig. 2c), indicating that some of the applied P was entering in this pool. However, the magnitude of the change was small, up to 80% in absolute values, highlighting the limited ability of this soil pool to retain added P compared to the labile P fraction. Again, there was no pattern of percentage of change between organic and mineral soils. With the exception of Galway peaty mineral soil, negative changes were measured for most of the P applications to the soils. The negative values in this fraction may be attributed to mineralization of the partially decomposed OM by the microbial community. It has been reported that mineralization of organic materials is enhanced by heterotrophic microorganisms when P is not a limiting element (Pisani et al., 2015; Wright and Reddy, 2001). Small P fertiliser additions may generate more plant available P derived from the mineralization of organic P fractions, so that this pool may play an important role in soil P fertility, acting as a source of plant available P in those soils where it is a relevant reservoir (Menezes-Blackburn et al., 2018; George et al., 2017; Condrón and Newman, 2011; Guo et al., 2000).

With the exception of Cork peaty mineral, where there was a tendency to build up P, changes in residual P (Fig. 2c) declined across P treatments. The low pH of the Cork peaty mineral soil may have favoured precipitation of some of the applied P with Fe and Al oxides that were part of the primary minerals in this soil. The reduction of the residual P pool in the rest of the soils (Fig. 2c) indicated that P may have been partially mineralized and therefore mobilised to other pools. The residual pool is considered the most recalcitrant and hence least available of all the fractions, as it is associated with very stable organo-metallic materials (Turner et al., 2005). However, previous research has shown that this pool can act as a source of P for arable crops and forest trees plantations in the short and long-term experiments under low or no P inputs (Velásquez et al., 2016; Condrón and Newman, 2011). To our knowledge, our results are the first to confirm this tendency under pasture (ryegrass) monoculture.

3.3. Pathways of transformations in soil P pools

Path analysis uses the data generated by the P fractionation technique in a theoretical model to differentiate between direct and indirect effects from one variable on others (Tiecher et al., 2018; Gama-Rodrigues et al., 2014; Kang et al., 2009; Zheng et al., 2004). These interrelations are evaluated as partial correlations between the variables but, unlike routine multiple regression analysis in which a single dependent variable is considered, path analysis conducts a multivariate multiple regression analysis where several dependent variables are subjected to regression analysis simultaneously on one or more independent variable. Unstandardized path coefficients are shown in Table 2 and in Figs. S1–S3 of the Supplementary material (standardized values are shown in Table S1 of the Supplementary material).

Phosphorus fertiliser had a significant impact on the majority of the soil P pools, although at different magnitudes. The labile P pool was significantly affected by P fertiliser applications in all the soils, with the highest effect in the most organic soils, with a $\beta = 0.70$ for Galway peat and $\beta = 0.27$ for Cork peaty mineral soil. This indicates that any added P in excess of plant requirements may pose an elevated risk of P transfer to surface waters in the organic soils under rainfall events in field

Table 2

Unstandardized partial regression coefficients. Direct (diagonal, bold) and indirect (off diagonal) contribution of P fertiliser applications on the different soil P pools. NS = not significant.

Variable	Residual	Ca-bound P	Organic P	Fe-Al bound P	Labile P
Galway peat					
Residual P	-0.49***				
Ca-bound P	NS	0.69***			
Organic P	-0.24*	NS	0.53***		
Fe-Al bound P	NS	NS	NS	0.55***	
Labile P	NS	NS	NS	NS	0.70***
Galway peaty mineral					
Residual P	1.12**				
Ca-bound P	-0.17*	1.27***			
Organic P	NS	0.94***	NS		
Fe-Al bound P	-0.43***	NS	NS	1.19***	
Labile P	0.08**	0.13**	NS	0.07**	0.15**
Cork mineral					
Residual P	NS				
Ca-bound P	NS	0.18***			
Organic P	-0.38***	NS	0.54***		
Fe-Al bound P	NS	1.62***	NS	0.46***	
Labile P	NS	NS	-0.10**	0.43***	0.09*
Cork peaty mineral					
Residual P	NS				
Ca-bound P	-0.13**	1.00***			
Organic P	NS	0.685*	0.85*		
Fe-Al bound P	NS	NS	NS	1.73***	
Labile P	0.08*	0.12*	0.03**	NS	0.27***
Wexford mineral					
Residual P	-0.55**				
Ca-bound P	-0.24*	0.29*			
Organic P	-0.25*	NS	0.45***		
Fe-Al bound P	NS	NS	NS	1.21***	
Labile P	NS	NS	NS	0.10*	0.25***
Wexford peaty mineral					
Residual P	NS				
Ca-bound P	-0.14**	0.17**			
Organic P	-0.18***	0.55***	0.38***		
Fe-Al bound P	NS	NS	0.58***	0.74***	
Labile P	NS	NS	NS	0.18***	0.04*

* Significant level at $p \leq 0.05$.

** Significant level at $p \leq 0.01$.

*** Significant level at $p \leq 0.001$.

conditions, as supported but Fig. 3.

The Fe-Al bound pool was a significant direct sink for freshly applied P for all the soils, as widely reported (Castillo and Wright, 2008; Zheng et al., 2004). Phosphorus fertiliser had the highest impact on the Fe-Al bound P in the Cork peaty mineral soil ($\beta = 1.73$), likely due to the very low pH of this soil that favoured immobilisation and physico-chemical sorption reactions between the freshly applied P and the amorphous and poorly crystalline Fe-Al oxides/hydroxides in this soil. The Fe-Al bound P pool contributed indirectly to the replenishment of labile P in most of the soils, especially in Cork mineral ($\beta = 0.46 \times 0.43$). However, there was no indirect relationship between added P and the labile pools through the Fe-Al bound P pool for the most organic soils (Galway peat, Cork peaty mineral). The lack of relationship between these two pools in these soils supports the idea that pH plays an important role in mobilisation reactions of P in soil.

The organic P pool had a considerable direct relationship with P fertiliser in all soils except Galway peaty mineral. The Cork peaty mineral soil had the highest response ($\beta = 0.85$). There was no substantial indirect effect of the organic pool to Fe-Al bound and labile P pools, with the exception of Wexford peaty mineral, where a moderate relationship between the organic P and Fe-Al bound P was calculated ($\beta = 0.58$; Table 2 and Fig. S3). These results show that P applications increased organic P reserves over short periods of time. Other studies reported a slight increase in the moderately labile organic P pools in

incubation and short-term (0 to ≤ 10 y) field studies (Negassa and Leinweber, 2009). However, as was reported in the previous section, the organic P pool experienced a negative change at low P rates in the majority of soils. These results highlight the potential role of the organic P pool as a source of P for plant uptake through mineralization when added P does not meet crop requirements for growth (Negassa and Leinweber, 2009; Castillo and Wright, 2008; Turner et al., 2007; Zheng et al., 2004). The role of the soil organic pools as a source of plant available P could be well evaluated in middle and long term unfertilised experiments by path analysis in future studies.

Phosphorus fertilisation had a large direct impact on the Ca-bound pools in all the soils, especially in Galway peaty mineral, Cork peaty mineral and Galway peat, with path coefficients of 1.27, 1.00 and 0.69, respectively. These soils had the highest Mehlich-III extracted Ca concentrations (Table 1), which may explain the higher affinity for P applied in this pool. The Ca-bound P pool exerted little indirect effect on the labile P across the different soils, but had a moderate influence in both organic and Fe-Al bound P pools, suggesting that mobilisation of P retained in this pool is possible but unlikely to become available, at least in the short-term. The hypothesis of partial mineralization of this relatively stable pool towards moderately labile fractions has been suggested in previous studies, which speculated that recalcitrant organic P included in this pool may be mineralized under aerobic conditions (Zheng et al., 2004; Guo et al., 2000; Schlichting et al., 2002).

Residual P showed a significant direct interaction with P fertiliser applications in half of the soils, with a negative effect in the Galway peat ($\beta = -0.49$) and Wexford mineral soils ($\beta = -0.55$), suggesting that this recalcitrant P can be mobilised when P is not limiting (Wright and Reddy, 2001). The residual P pool was an important sink for the P applied in Galway peaty mineral, as indicated by the large positive direct effect of the path coefficient ($\beta = 1.12$). Although not statistically significant ($p > 0.05$), the path coefficients in Cork mineral and Wexford peaty mineral soils were also negative (data not shown), indicating an overall tendency of the P retained in this pool to be mobilised and become a potential source of P for plant growth.

When the different pathways of P transformations are compared considering the amount of OM of the soils used in this study, there were no significant transformations among the soil pools in the soil with the highest OM content (Galway peat, 76% OM). Likewise, Cork peaty mineral, the second largest in OM content (66%), had limited transformations among its pools, with relatively low enrichment of the labile pool via the Ca-bound P pool ($\beta = 1.0 \times 0.12$) and the organic P pool ($\beta = 0.85 \times 0.03$). Plant growth in these two soils may be restricted under low or nonfertilised management regimes due to their limited ability to replenish labile P, leaving them dependent on continuous fertilisation. On the other hand, added P was indirectly transformed into moderately labile Fe-Al bound P pools to a greater extent in mineral soils, indicating an enhanced ability to build up P reserves compared to organic soils, and were therefore more resilient to nonfertilised management regimes. However, this trend in mineral and organic soils is likely to be so due to the short length of this experiment, and further work in medium and long-term field conditions should be conducted.

4. Conclusions

Under P deficient scenarios, this work showed that external P additions accumulated mainly in the labile P pool across the different soil types, followed by the Fe-Al bound P pool. However, organic soils displayed a more limited ability to build-up labile P and, to a lesser extent, Fe-Al bound P reserves, compared to mineral soils, rendering them vulnerable to P losses when fertiliser is applied in excess of the crop requirements for growth. Additionally, there was a higher P uptake in the grass yield of these organic soils than in mineral soils, indicating that P fertiliser applications to P-deficient organic soils tend to remain in the soil solution and therefore should be restricted to growing periods when there is a demand for P and the risk of precipitation is

low. Soil pH should be optimized prior any fertilisation event, even in P deficient soils, as it influences the retention of applied P. Organic and residual P pools were partially mineralized in most of the soils, indicating mobilisation towards more labile pools. Therefore, they may be considered as a potential source of P for plants.

Transformations of P between the different P pools under fertilisation were well explained by path analysis, and showed the potential of the more recalcitrant pools to mobilise P into more labile P in all the soils. Only the most OM-rich soil had no significant P turnover from the more recalcitrant to labile pools, rendering it dependent to external P applications that may elevate the risk of incidental P losses. Current fertiliser recommendations are mostly based on single agronomic soil P tests that only measure readily available P in the labile P pool, but do not take into consideration the interrelationships with recalcitrant P pools, which may be a potential source of P.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2018.11.049>.

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