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Title	Effects of fertiliser on phosphorus pools in soils with contrasting organic matter content: A fractionation and path analysis study
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Publication Date	2018-12-05
Publication Information	González Jiménez, J. L., Healy, M. G., & Daly, K. (2019). Effects of fertiliser on phosphorus pools in soils with contrasting organic matter content: A fractionation and path analysis study. Geoderma, 338, 128-135. doi: https://doi.org/10.1016/j.geoderma.2018.11.049
Publisher	Elsevier
Link to publisher's version	https://doi.org/10.1016/j.geoderma.2018.11.049
Item record	http://hdl.handle.net/10379/14738
DOI	http://dx.doi.org/10.1016/j.geoderma.2018.11.049

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Published as: González Jiménez, J.L., Healy, M.G., Daly, K. 2019. Effects of fertiliser on phosphorus
 pools in soils with contrasting organic matter content: a fractionation and path analysis study.
 Geoderma 338: 128-135. https://doi.org/10.1016/j.geoderma.2018.11.049

5 Effects of fertiliser on phosphorus pools in soils with contrasting organic matter content: A fractionation and path analysis study 6 7 J.L. González Jiménez^{a, b}, M.G. Healy^b, K. Daly^a 8 9 ^a Teagasc, Johnstown Castle, Environment Research Centre, Co Wexford, Rep. of Ireland, 10 ^bCivil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of Ireland 11 12 Abstract 13 With the intensification of agricultural production in many European countries, more 14 marginal soils with elevated organic matter (OM) content are being brought into cultivation. 15 However, little is known about the transformations in the constituent phosphorus (P) pools of 16 organic soils receiving applications of P fertiliser. Soil P fractions were measured before and 17 after receiving fertiliser in a controlled experiment to determine the change in the soil pools 18 and path analysis was used to evaluate the relationships between P pools. In this study, P 19 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 20 21 monitored over an eight-month study period. High OM soils had a diminished ability to 22 build-up the labile pool from freshly applied P, with relatively low increases up to 200 % of 23 the initial value, compared to mineral soils in which the labile pool increased to more than 24 2500 % of the initial concentration. Additionally, organic soils had higher P uptakes in the 25 grass yield than mineral soils, indicating a higher availability of added P in the soil solution 26 than mineral soils due to their limited sorption ability. In general, there was a reduction in the 27 organic P pool over applications from 0 to 55 kg ha⁻¹, which was indicative of partial 28 mineralisation, but was followed by an accumulation of added P over applications from 55 to 29 145 kg P ha⁻¹. The residual P pools did not build-up with P additions, but data indicated the 30 occurrence of mineralisation in most of the soils with decreases of around 40 % of the initial 31 concentrations. Organic and residual pools therefore displayed potential to supply P to more 32 labile P pools across all soils of this study. Path analysis indicated that applied P was the only 33 source of labile P in the soil with the highest OM content, leaving it dependant on continuous 34 P applications to supply P for productivity, whereas in the rest of the soils there were 35 interrelations between the non-labile and labile pools. Low pH strongly immobilised the 36 applied P and should be corrected before the initiation of any fertilisation program, even in 37 soils deficient in plant available P. The results demonstrated that P added as fertiliser to 38 organic soils does not accumulate as in mineral soils, which may leave them susceptible to P 39 losses in surface runoff. Therefore, organic soils under agricultural production located in high 40 status catchments should receive low P applications and only during periods with low 41 probability of precipitation to minimise the possibility of P exports to receiving waters.

42

43 Keywords

44 P fractions; Build-up; Histosols; Hedley fractionation; Soil P cycling; Pathways.

45

46 Introduction

47 The maintenance of grasslands for livestock production often requires the application of

48 nutrients in the form of fertilisers to balance the exports derived from that productivity.

49 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).

54 Histosols and other peat-derived soil, often described as organic soils (Creamer et al., 2014), 55 typically contain large amounts of organic matter (OM) at the surface and have poor P 56 retention capacities (Guppy et al., 2005; Daly et al., 2001). With a total land area of 57 approximately 7 % in Europe (Montanarella et al., 2006), organic soils have received 58 relatively little attention regarding P management. In the Republic of Ireland, approximately 59 840,000 ha of organic soils are currently or potentially under agricultural production (Renou-60 Wilson et al., 2011). Many of these soils are located in upland, remote areas and set within 61 high ecological status or pristine water bodies identified under the European Water 62 Framework Directive (OJEC, 2000). This regulation encourages member states to maintain 63 "high" ecological water status where it exists and to achieve at least "good" ecological status 64 for all water bodies. However, with the intensification of agricultural practices across Europe, 65 these sites often receive high P inputs similar to those usually applied in areas under intensive 66 livestock production (Roberts et al., 2017), and recent studies have linked the loss of "high 67 ecological status" in these catchments to these practices (White et al., 2014). Therefore, it is 68 essential to understand the impact of fertiliser applications on the P chemistry in organic soils 69 and to evaluate possible negative effects of P management, if the quality of the sensitive 70 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;

75 Porter and Sanchez, 1992). Phosphorus fertiliser recommendations on mineral soils are based 76 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 77 78 (Voss, 1998; Olson et al., 1987). However, the ability of organic soils to sorb and retain P 79 applied is impeded by the inherent large amounts of OM that compete for sorption sites 80 (Guppy et al., 2005; Daly et al., 2001), so that the approach of build-up of P and maintenance 81 on these soils for fertiliser recommendations has been questioned (Roberts et al., 2017; Daly 82 et al., 2015).

83 The sequential P fractionation procedure, developed by Hedley et al. (1982), extracts P bound 84 from diverse inorganic and organic compounds of different lability using solutions of 85 increasing extracting strength (Cross and Schlesinger, 1995). Despite its limitations when 86 providing P speciation at the P fraction level and the likelihood to overestimate organic P 87 (Turner et al., 2005), the Hedlev method is one of the most comprehensive methodologies 88 used to evaluate the soil P cycle and dynamics into "operationally-defined fractions" of 89 different availability and nature (Condron and Newman, 2011; Negassa and Leinweber, 90 2009). However, only a few studies have applied this technique in OM-rich soils (Schlichting 91 et al., 2002; Cross and Schlesinger, 1995) and, to our knowledge, none exists in organic soils 92 where the effect of P applied in the different soil P pools has been evaluated using this 93 technique. Therefore, there is a lack of knowledge about the interaction of freshly applied P 94 with the different soil P fractions when organic acids are in direct competition for the same 95 reaction sites as the P applied. Phosphorus assimilation and turnover in agricultural organics 96 soils is poorly understood and needs further research in order to improve their management 97 and minimise potential P loses to the environment.

98 Sequential P fractionation techniques alone do not provide insight on the relationships and
99 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.

111

112 Materials and methods

113 Pot experiment

114 Six grassland soils deficient in P and representing a range of OM content, were selected from 115 three high status catchments in the Republic of Ireland (Table 1). All soils were under a low 116 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 117 118 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 119 120 taken from each soil and analysed for selected physico-chemical properties and to determine 121 initial P concentrations in the different P pools defined below (Table 1).

122 Soils were rewetted to their field gravimetric water content and placed in 18.5 L pots (0.3 m 123 upper diameter, 0.3 deep). Each soil received fourteen P fertiliser applications (n=2) as single 124 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 125 126 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 127 perenne L.) seeds at a rate equivalent to 28 g m⁻² and placed in a glasshouse for three months 128 under the following conditions: average temperature of 11.1° C (±3.9° C) and relative 129 130 humidity of 82 % (± 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 131 night-time temperatures of 8° C, with respectively relative humidities of 85 % and 75 %, and 132 (3) photosynthetically active radiation of $450 \pm 50 \text{ }\mu\text{mol} \text{ }\text{m}^{-2}\text{s}^{-1}$. The pots were randomly 133 placed in the chambers and were held between 60 to 90 % field capacity by weighting them 134 135 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 136 days, composited and subjected to soil P fractionation analysis. Phosphorus use efficiency 137 138 and magnitude of grass response to P fertilisations in these soils were evaluated, the details of 139 which are in González Jiménez et al (in press).

140

141 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 146 test is more suitable for soils of different nature as its ability to determine dissolved and 147 loosely bound P is not influenced by physical or chemical properties of the soils (Robinson 148 and Sharpley, 1994). Duplicate 0.5 g samples of dried soil were weighed in 50 mL 149 polypropylene tubes and shaken in 40 mL of 0.01 M CaCl₂ with iron-oxide paper strips for 16 150 h using a reciprocal shaker operated at 6 rpm. Phosphorus adsorbed to the iron strips was 151 dissolved by shaking the strips for 1 h in 40 ml 0.1 M H₂SO₄. This fraction was identified as 152 the FeO strip-P. The soil suspension was then centrifuged at approximately 51845 m s⁻¹ for 153 20 min and the supernatant was decanted. The soil was then sequentially extracted with: (1) 154 30 ml of 0.5 M NaHCO₃ at pH 8.5 (NaHCO₃-P) (2) 0.1 M NaOH (NaOH-P), and (3) 1 M 155 H₂SO₄ (H₂SO₄-P), each of them at the same shaking and centrifuging settings as described for 156 the FeO strip-P. The residual P fraction resisting the 1 M H₂SO₄ extraction was calculated as 157 the difference between total P (P_t) and the sum of FeO strip-P + NaHCO₃-P + NaOH-P + H₂SO₄-P. Total P was determined by ICP-OES in a separate 0.5 g dried sample using the 158 159 microwave-assisted acid digestion method (USEPA, 1996). Inorganic P (Pi) concentrations 160 for all the extractants were determined within 24 h using the ascorbic acid-molybdenum blue 161 method (Kuo, 1996). The Pt concentration in the different extractants (except for the FeO 162 strip-P, where only P_i was determined) was determined by acid potassium persulfate digestion. Organic P concentrations (Po) in the NaHCO3 and NaOH fractions were calculated 163 164 as the difference between P_t and P_i.

165

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 NaHCO₃-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 NaHCO₃-P_o + NaOH-P_o represented the organic P pool (4) the H₂SO₄-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 (GamaRodrigues et al., 2014; Condron and Newman, 2011; Negassa and Leinweber, 2009;
Schlichting et al., 2002; Cross and Schlesinger, 1995).

177

178 Statistical analysis

179 In order to analyse and evaluate the impact of the increasing P fertiliser applications on the 180 different soil P pools, the percentage change for each soil and P pool were calculated as the 181 difference between the P concentration after and before the experiment divided by the 182 original P concentration. Path analysis was used to examine the cause-and-effect relationships 183 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 184 185 dose (kg ha⁻¹) for each soil pool the end of the experiment were used in the path analysis. The conceptual diagram in Figure 1 was proposed as a general model to test P transformations 186 187 and dynamics in the different soils. Phosphorus fertiliser was the sole independent variable 188 that may affect the different soil P pools. Therefore, the soil P pools were considered as 189 dependent variables. A basic assumption of the model is that, under cultivation conditions 190 where soils are mainly aerated most time of the year, P movements between the soil P pools 191 occur from the most recalcitrant pools to the less recalcitrant ones and not vice-versa, as 192 might happen under flooded conditions where the redox conditions would change (Castillo 193 and Wright, 2008). This is represented in the model by the different arrows between the 194 independent variable and the dependent variables, and within the dependent variables 195 following the assumption mentioned above (Figure 1). Each potential relationship in the

196 model (cause) is measured by a partial regression coefficient (direct effect). They are 197 analogous to the covariance between two variables and are referred to as path coefficients (β). 198 Indirect effects are referred to as the effects between two variables that are mediated by 199 another intervening variable (Raykov and Marcoulides, 2006). Both unstandardized (raw 200 score units) and standardized (standard deviation units) path coefficients were calculated. The 201 use of unstandardized path coefficients enabled comparison for the same variable relationship 202 across the different soils, whereas standardized path coefficients were better for comparing 203 different variable relationships within the same soil (Beaujean, 2014).

204 The generic model represented in Figure 1 is a saturated model with zero degrees of freedom, 205 that is, there are as many estimated parameters as data points (observations). By definition, 206 saturated models exhibit perfect fit to the data and hence they cannot be confirmed or 207 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 208 209 freedom could be tested. Modifications of the saturated model were done by dropping from 210 the model the non-significant path coefficients stepwise until final models were tenable, 211 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 212 213 used to validate the nested model from the preceding one until the most restrictive, yet 214 plausible, model was achieved for each soil (Raykov and Marcoulides, 2006). Comparative 215 Fit Index (CFI), Expected Cross Validation Index (ECVI), Akaike's Information Criterion 216 (AIC), and Goodness of Fit Index (GFI) were also considered to evaluate the fit strength of 217 the models generated. Analyses were carried out in R statistical software, version 3.4.2 (R 218 Core Team, 2017) using the "lavaan" and "semPlot" packages (Epskamp, 2017; Rosseel, 219 2012).

220

221 Results and discussion

222 Soils characterization

The physico-chemical characteristics of the soils before the application of fertiliser are shown 223 224 in Table 1. The range of OM content reflects a broad variation, spanning from 8.7 to 76.4 %, 225 representing the contrasting soil types in high status catchments in Ireland (White et al., 226 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. 227 228 Total P in the soils ranged between 369.1 to 1174.2 mg kg⁻¹. From a pedogenic point of view, 229 Galway peat, classified as Ombric Histosol, had similar values to those reported by Yang and 230 Post (2011), but less than other semi-natural or cultivated Histosols reported elsewhere 231 (Schlichting et al., 2002). The other soils in this study had considerably larger Pt 232 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, 233 indicating that pH favoured retention of P in this stable fraction from past P additions 234 (Castillo and Wright, 2008; Schlichting et al., 2002). There were no other significant 235 236 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 50.4 237 238 % and from 25.4 to 55.3 % of the P_t, respectively, whereas labile P was the smallest fraction 239 and did not exceed 5.5 % of the P_t in any soil (Table 1).

240

241 Changes in P pools over the study duration

242 Figure 2 shows the percentage change before and after the pot study in labile P, Fe-Al-bound 243 P, Ca-bound P, organic P and residual P pools in each soil over all P applications. The labile 244 P fraction (Figure 2a) increased with increasing rates of P applications in all the soils, as 245 expected. Part of the P applied in the form of fertiliser was taken up by the grass, while the 246 rest reacted with the soil matrix and was adsorbed to soil particles. There were negative 247 changes in labile P in Galway peat, Cork peaty mineral and, to a lesser extent, Galway peaty 248 mineral and Wexford mineral, until P applications exceeded threshold values of 249 approximately 45, 35, 25 and 10 kg ha⁻¹, respectively, indicating a partial depletion of the 250 original pool by grass growth and uptake. Here, grass growth may have been impeded due to 251 lack of available P, until the rates of application were enough to support plant growth and 252 replenish the labile P pool. Galway peat and Cork peaty mineral, the soils with the most OM 253 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 254 255 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 256 257 retain freshly applied P into this fraction. Therefore, high percentage change values mean that 258 large amounts of added P ended up in this pool, whereas low values indicate that only a small 259 amount was tied up here. Phosphorus concentration in the soil solution phase immediately 260 after fertiliser applications is typically very high (saturated solution), and undergoes rapid 261 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 262 263 (McLaughlin et al., 2011). Mineral soils demonstrated a high ability to adsorb P in the surface 264 areas of their mineral fraction, whereas this adsorption capacity in organic soils was much 265 smaller (Figure 2a).

266 Phosphorus not retained in the labile pool of the organic soils was taken up by the plant roots 267 in higher proportions than in mineral soils, as P was readily available in the soil solution and 268 not loosely bound to soil mineral particles. This was evidenced by the higher P uptakes of the 269 organic soils compared to mineral soils (Figure 3). At high P doses, when it is likely that P 270 has been applied in excess of crop requirements, organic soils with a low % change in labile 271 P showed higher P uptake by the plant roots compared to mineral soils with higher % changes 272 but lower P uptake (Figure 3). The fertiliser and agronomic responses of this trial are detailed 273 in González Jiménez et al. (in press). Organic soils have low sorption and retention 274 capacities for P (Guppy et al., 2005, Daly et al., 2001), so the relative inability of these soils 275 to retain P applied in excess of crop requirements increases the risk of P loss to the aquatic 276 environment (Roberts et al., 2017; Daly et al., 2001). The iron-oxide paper strip method, used 277 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 278 279 molecule among the organic P compounds, it is relatively resistant to mineralisation. 280 However, it is likely that other more degradable molecules, such as phospholipids and nucleic 281 acids, are more abundant in organic soils and therefore prone to be mineralised in the 282 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 283 284 of labile P pools, diffusive gradients in thin films (Zhang et al., 2014; Ding et al., 2010) could 285 be used in future studies to efficiently estimate bioavailable P, especially in organic soils 286 where degradable organic P is likely to be present in a higher proportion compared to mineral 287 soils.

The Fe-Al bound and Ca-bound P fractions increased proportionally to the P applications in all the soils (Figure 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

291 measured in the Fe-Al bound P in the mineral soils (Cork mineral and Wexford peaty 292 mineral). The short duration of this study likely hindered a better observation of any potential 293 trend between organic and mineral soils. None of the soils had negative percentage changes, 294 indicating that there was no depletion of these pools at low P doses during the experiment. 295 With the exception of Cork peaty mineral, the magnitude of change in the Ca-bound P 296 fraction was smaller than the Fe-Al bound P, supporting the hypothesis that this pool is 297 considered a more stable fraction to short-term changes and least reactive to freshly applied P 298 (Cross and Schlesinger, 1995). With no P applied (zero P rate), the percentage of change in 299 these two fractions was positive at the end of the experiment, indicating that P was released 300 from other pools and retained in these fractions. Likely, part of the P contained in the organic 301 P and residual P fractions was mineralized and transferred to these pools.

302 There was a build-up in the organic P pool across the P treatments (Figure 2c), indicating that 303 some of the applied P was entering in this pool. However, the magnitude of the change was 304 small, up to 80 % in absolute values, highlighting the limited ability of this soil pool to retain 305 added P compared to the labile P fraction. Again, there was no pattern of percentage of 306 change between organic and mineral soils. With the exception of Galway peaty mineral soil, 307 negative changes were measured for most of the P applications to the soils. The negative 308 values in this fraction may be attributed to mineralization of the partially decomposed OM by 309 the microbial community. It has been reported that mineralization of organic materials is 310 enhanced by heterotrophic microorganisms when P is not a limiting element (Pisani et al., 311 2015; Wright and Reddy, 2001). Small P fertiliser additions may generate more plant 312 available P derived from the mineralization of organic P fractions, so that this pool may play 313 an important role in soil P fertility, acting as a source of plant available P in those soils where 314 it is a relevant reservoir (Menezes-Blackburn et al., 2018; George et al., 2017; Condron and 315 Newman, 2011; Guo et al., 2000).

316 With the exception of Cork peaty mineral, where there was a tendency to build up P, changes 317 in residual P (Figure 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 318 319 were part of the primary minerals in this soil. The reduction of the residual P pool in the rest 320 of the soils (Figure 2c) indicated that P may have been partially mineralized and therefore 321 mobilised to other pools. The residual pool is considered the most recalcitrant and hence least 322 available of all the fractions, as it is associated with very stable organo-metallic materials 323 (Turner et al., 2005). However, previous research has shown that this pool can act as a source 324 of P for arable crops and forest trees plantations in the short and long-term experiments under 325 low or no P inputs (Velásquez et al., 2016; Condron and Newman, 2011). To our knowledge, 326 our results are the first to confirm this tendency under pasture (ryegrass) monoculture.

327

328 Pathways of transformations in soil P pools

329 Path analysis uses the data generated by the P fractionation technique in a theoretical model 330 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 331 332 interrelations are evaluated as partial correlations between the variables but, unlike routine 333 multiple regression analysis in which a single dependent variable is considered, path analysis 334 conducts a multivariate multiple regression analysis where several dependent variables are 335 subjected to regression analysis simultaneously on one or more independent variable. Unstandardized path coefficients are shown in Table 2 and in Figures S1-S3 of the 336 supplementary material (standardized values are shown in Table S1 of the supplementary 337 338 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 conditions, as supported but figure 3.

The Fe-Al bound pool was a significant direct sink for freshly applied P for all the soils, as 345 346 widely reported (Castillo and Wright, 2008; Zheng et al., 2004). Phosphorus fertiliser had the 347 highest impact on the Fe-Al bound P in the Cork peaty mineral soil ($\beta = 1.73$), likely due to 348 the very low pH of this soil that favoured immobilization and physico-chemical sorption 349 reactions between the freshly applied P and the amorphous and poorly crystalline Fe-Al 350 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 ($\beta = 0.46 \times 0.43$). 351 352 However, there was no indirect relationship between added P and the labile pools through the 353 Fe-Al bound P pool for the most organic soils (Galway peat, Cork peaty mineral). The lack of 354 relationship between these two pools in these soils supports the idea that pH plays an important role in mobilization reactions of P in soil 355

356 The organic P pool had a considerable direct relationship with P fertiliser in all soils except 357 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, 358 359 with the exception of Wexford peaty mineral, where a moderate relationship between the 360 organic P and Fe-Al bound P was calculated ($\beta = 0.58$; Table 2 and Figure S3). These results 361 show that P applications increased organic P reserves over short periods of time. Other 362 studies reported a slight increase in the moderately labile organic P pools in incubation and 363 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.

371 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 372 373 coefficients of 1.27, 1.00 and 0.69, respectively. These soils had the highest Mehlich-III 374 extracted Ca concentrations (Table 1), which may explain the higher affinity for P applied in 375 this pool. The Ca-bound P pool exerted little indirect effect on the labile P across the different 376 soils, but had a moderate influence in both organic and Fe-Al bound P pools, suggesting that 377 mobilization of P retained in this pool is possible but unlikely to become available, at least in 378 the short-term. The hypothesis of partial mineralisation of this relatively stable pool towards 379 moderately labile fractions has been suggested in previous studies, which speculated that 380 recalcitrant organic P included in this pool may be mineralised under aerobic conditions 381 (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 forplant growth.

391 When the different pathways of P transformations are compared considering the amount of 392 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 393 394 mineral, the second largest in OM content (66 %), had limited transformations among its 395 pools, with relatively low enrichment of the labile pool via the Ca-bound P pool ($\beta = 1.0 \text{ x}$ 396 0.12) and the organic P pool ($\beta = 0.85 \times 0.03$). Plant growth in these two soils may be 397 restricted under low or nonfertilized management regimes due to their limited ability to 398 replenish labile P, leaving them dependant on continuous fertilisation. On the other hand, 399 added P was indirectly transformed into moderately labile Fe-Al bound P pools to a greater 400 extent in mineral soils, indicating an enhanced ability to build up P reserves compared to 401 organic soils, and were therefore more resilient to nonfertilised management regimes. 402 However, this trend in mineral and organic soils is likely to be so due to the short length of 403 this experiment, and further work in medium and long-term field conditions should be 404 conducted.

405

406 **Conclusions**

407 Under P deficient scenarios, this work showed that external P additions accumulated mainly

408 in the labile P pool across the different soil types, followed by the Fe-Al bound P pool.

409 However, organic soils displayed a more limited ability to build-up labile P and, to a lesser

- 410 extent, Fe-Al bound P reserves, compared to mineral soils, rendering them vulnerable to P
- 411 losses when fertiliser is applied in excess of the crop requirements for growth. Additionally,
- 412 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.

419 Transformations of P between the different P pools under fertilisation were well explained by 420 path analysis, and showed the potential of the more recalcitrant pools to mobilise P into more 421 labile P in all the soils. Only the most OM-rich soil had no significant P turnover from the 422 more recalcitrant to labile pools, rendering it dependent to external P applications that may 423 elevate the risk of incidental P losses. Current fertiliser recommendations are mostly based on 424 single agronomic soil P tests that only measure readily available P in the labile P pool, but do 425 not take into consideration the interrelationships with recalcitrant P pools, which may be a 426 potential source of P.

427

428 Acknowledgments

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. José L. González Jiménez was funded by the Teagasc Walsh Fellowship Scheme. The authors would like to thank the landowners for generously providing the soils used in this study, and the support and assistance of D. Brennan, L Moloney Finn and I. Marongiu for their support and advice in the use of Teagasc Johnstown Castle laboratories. We would also like to thank the editor and two anonymous reviewers for their critical and helpful comments and suggestions.

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Soil property	Units	Galway peat	Galway peaty mineral	Cork mineral	Cork peaty mineral	Wexford mineral	Wexford peaty mineral
Classification*		Ombric 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
pН		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)
Р		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)

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.

* World Reference Base 2014 (IUSS Working Group WRB, 2014)

Table 2. Unstandardized partial regression coefficients. Direct (diagonal, bold) and indirect (off diagonal) contribution of P fertiliser applications on the different soil P pools. Significant levels at $p \le 0.05$, 0.01 and 0.001 represented by ^{*}, ^{**} and ^{***}, respectively. NS = not significant.

Variable	Residual	Ca-bound P	Organic P	Fe-Al bound P	Labile P
		G	alway 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	y Peaty Min	eral	
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**
		Со	rk 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 Mine	al	
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***
		Wex	ford Minera	ıl	
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***
		Wexfor	d Peaty Min	eral	
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*

Figure 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)



1 Figure 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, \bullet symbol) and Residual P (right vertical axis, \star symbol) fractions across P applications in the six solid studied. Dereentages represent the organic metter content

3 the six soils studied. Percentages represent the organic matter content.

4



Figure 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.

