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4

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

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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
20 ryegrass and subjected to P fertiliser applications ranging from 10 to 145 kg ha⁻¹, and
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

50 essential contribution to plant growth, but also for its complex chemistry within the soil
51 matrix (Epstein and Bloom, 2004; Pierzynski and McDowell, 2005). When applied in excess
52 of the crop requirements, P accumulates in soil which may increase the risk of P losses to
53 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.

71 Phosphorus applied to soils undergoes a series of physico-chemical (dissolution-precipitation
72 and desorption-adsorption) transformations regulated by soil characteristics such as
73 mineralogy composition, surface area, pH, extractable iron-aluminium (Fe-Al) hydroxides
74 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,
77 followed by the maintenance of that level by replacing the P removed by consecutive harvests
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 Hedley 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 (Condrón 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 losses 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

100 comparison of soils of different pedogenesis receiving the same treatments (Gama-Rodrigues
101 et al., 2014; Zheng et al., 2004). Path analysis has been shown to be a valuable tool to
102 evaluate the cause-and-effect interrelations between P pools in different soil types and under
103 a variety of management regimes (Tiecher et al., 2018; Zheng et al., 2004; Beck and Sanchez,
104 1994; Tiessen et al., 1984).

105 Therefore, the objectives of this study were (1) to assess the changes in the different soil P
106 fractions receiving increasing amounts of P fertiliser, and (2) to examine which pools acted as
107 sinks or sources for P so as to gain a better understanding of the soil P cycle. To address these
108 objectives, six soils deficient in available P and ranging in OM content were placed in large
109 pots and received fourteen increasing amounts of P fertiliser under ryegrass growth, and were
110 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,
117 with the exception of Galway peaty mineral, which received P applications of approximately
118 32 kg P ha⁻¹y⁻¹ in the years prior to the soil collection. The soils were collected from the
119 surface horizon (0-20 cm), air dried, and sieved through a 12 mm mesh. A subsample was
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,
125 55, 70, 100 and 145 kg P ha⁻¹. Each pot received an initial application of nitrogen (N) as
126 calcium ammonium nitrate and potassium (K) as potassium chloride, at a rate equivalent to
127 55 kg ha⁻¹ and 245 kg ha⁻¹, respectively. Pots were sown with perennial ryegrass (*Lolium*
128 *perenne* L.) seeds at a rate equivalent to 28 g m⁻² and placed in a glasshouse for three months
129 under the following conditions: average temperature of 11.1° C (±3.9° C) and relative
130 humidity of 82 % (± 12 %). Pots were then placed in controlled growth chambers operated in
131 the following conditions: (1) photoperiod of 16 h light (2) daytime temperatures of 14° C and
132 night-time temperatures of 8° C, with respectively relative humidities of 85 % and 75 %, and
133 (3) photosynthetically active radiation of 450 ± 50 μmol m⁻²s⁻¹. The pots were randomly
134 placed in the chambers and were held between 60 to 90 % field capacity by weighting them
135 regularly. The grass was harvested six times when it attained a length of 22-26 cm. At the end
136 of the experiment, and for each pot, six soil cores were taken, oven-dried at 40 °C for three
137 days, composited and subjected to soil P fractionation analysis. Phosphorus use efficiency
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*

142 A modified Hedley fractionation procedure (Hedley et al., 1982) was used for each soil and P
143 treatment to determine the different fractions before and after the experiment. The iron-oxide
144 paper strip method (Menon et al., 1989) was used as an alternative to the traditionally used
145 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 CaCl_2 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 H_2SO_4 . 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 NaHCO_3 at pH 8.5 ($\text{NaHCO}_3\text{-P}$) (2) 0.1 M NaOH (NaOH-P), and (3) 1 M
155 H_2SO_4 ($\text{H}_2\text{SO}_4\text{-P}$), 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 H_2SO_4 extraction was calculated as
157 the difference between total P (P_t) and the sum of FeO strip-P + $\text{NaHCO}_3\text{-P}$ + NaOH-P +
158 $\text{H}_2\text{SO}_4\text{-P}$. Total P was determined by ICP-OES in a separate 0.5 g dried sample using the
159 microwave-assisted acid digestion method (USEPA, 1996). Inorganic P (P_i) concentrations
160 for all the extractants were determined within 24 h using the ascorbic acid-molybdenum blue
161 method (Kuo, 1996). The P_t concentration in the different extractants (except for the FeO
162 strip-P, where only P_i was determined) was determined by acid potassium persulfate
163 digestion. Organic P concentrations (P_o) in the NaHCO_3 and NaOH fractions were calculated
164 as the difference between P_t and P_i .

165

166 The different chemically extracted fractions were grouped into operationally defined pools of
167 increasing recalcitrance as follows: (1) the FeO strip-P represented the labile P pool and
168 comprised P dissolved in the soil solution along with loosely adsorbed P (2) the $\text{NaHCO}_3\text{-P}_i$
169 and NaOH-P_i represented the Fe-Al bound P pool and included moderately sorbed and/or
170 fixed P_i by Al and Fe oxides/hydroxides (3) analogous to the Fe-Al bound P, the $\text{NaHCO}_3\text{-P}_o$

171 + NaOH-P_o represented the organic P pool (4) the H₂SO₄-P represented the Ca-bound P pool
172 and comprised stable P contained in primary minerals such as apatite (5) the residual P pool,
173 calculated as the difference between the P_t and the sum of the previous pools, comprised
174 highly stable organometallic complexes and organic materials such as lignin (Gama-
175 Rodrigues et al., 2014; Condron and Newman, 2011; Negassa and Leinweber, 2009;
176 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
184 effects of these relationships. Phosphorus concentrations (in mg kg⁻¹) at each P application
185 dose (kg ha⁻¹) for each soil pool the end of the experiment were used in the path analysis. The
186 conceptual diagram in Figure 1 was proposed as a general model to test P transformations
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
208 used as a benchmark against which nested (modified) models with positive degrees of
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
212 plausible variable was excluded. The Chi square test (χ^2), at a significance level of 0.05, was
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*

223 The physico-chemical characteristics of the soils before the application of fertiliser are shown
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
227 of 4.5, 5.1 and 5.3, respectively, in contrast with near-to-neutral values for the other soils.
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 P_t
232 concentrations compared to those in the Yang and Post (2011) pedogenic study. There was a
233 significant positive correlation ($r^2 = 0.7$, $p < 0.05$) between soil pH and Ca-bound P fraction,
234 indicating that pH favoured retention of P in this stable fraction from past P additions
235 (Castillo and Wright, 2008; Schlichting et al., 2002). There were no other significant
236 correlations between the remaining fractions and other soil properties. Organic P and residual
237 P were by far the predominant fractions in all the soils, with values ranging from 24.2 to 50.4
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
254 %), whereas more mineral soils, such as Wexford peaty mineral and Cork mineral, had
255 maximum positive percentage changes exceeding 2500 %. The magnitude at which the labile
256 P pool changed across the P applications is an indication of the ability of each soil to sorb and
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
262 decreasing its concentration to levels typically very small compared to the solid phases
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
278 (Robinson and Sharpley, 1994). Although inositol hexaphosphate is the predominant
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;
283 Ivanoff et al., 1998). To minimise this potential source of error and improve the interpretation
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.

288 The Fe-Al bound and Ca-bound P fractions increased proportionally to the P applications in
289 all the soils (Figure 2b). There was no clear pattern of P accumulation across the different
290 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; Condon 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
318 soil may have favoured precipitation of some of the applied P with Fe and Al oxides that
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; Condon 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.,
331 2018; Gama-Rodrigues et al., 2014; Kang et al., 2009; Zheng et al., 2004). These
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.
336 Unstandardized path coefficients are shown in Table 2 and in Figures S1-S3 of the
337 supplementary material (standardized values are shown in Table S1 of the supplementary
338 material).

339 Phosphorus fertiliser had a significant impact on the majority of the soil P pools, although at
340 different magnitudes. The labile P pool was significantly affected by P fertiliser applications
341 in all the soils, with the highest effect in the most organic soils, with a $\beta = 0.70$ for Galway
342 peat and $\beta = 0.27$ for Cork peaty mineral soil. This indicates that any added P in excess of
343 plant requirements may pose an elevated risk of P transfer to surface waters in the organic
344 soils under rainfall events in field conditions, as supported but figure 3.

345 The Fe-Al bound pool was a significant direct sink for freshly applied P for all the soils, as
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
351 replenishment of labile P in most of the soils, especially in Cork mineral ($\beta = 0.46 \times 0.43$).
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
355 important role in mobilization reactions of P in soil

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 ($\beta = 0.85$).
358 There was no substantial indirect effect of the organic pool to Fe-Al bound and labile P pools,
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

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

371 Phosphorus fertilisation had a large direct impact on the Ca-bound pools in all the soils,
372 especially in Galway peaty mineral, Cork peaty mineral and Galway peat, with path
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)

382 Residual P showed a significant direct interaction with P fertiliser applications in half of the
383 soils, with a negative effect in the Galway peat ($\beta = -0.49$) and Wexford mineral soils ($\beta = -$
384 0.55), suggesting that this recalcitrant P can be mobilised when P is not limiting (Wright and
385 Reddy, 2001). The residual P pool was an important sink for the P applied in Galway peaty
386 mineral, as indicated by the large positive direct effect of the path coefficient ($\beta = 1.12$).
387 Although not statistically significant ($p > 0.05$), the path coefficients in Cork mineral and
388 Wexford peaty mineral soils were also negative (data not shown), indicating an overall

389 tendency of the P retained in this pool to be mobilised and become a potential source of P for
390 plant 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
393 pools in the soil with the highest OM content (Galway peat, 76 % OM). Likewise, Cork peaty
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 ($\beta = 1.0 \times$
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,

413 indicating that P fertiliser applications to P-deficient organic soils tend to remain in the soil
414 solution and therefore should be restricted to growing periods when there is a demand for P
415 and the risk of precipitation is low. Soil pH should be optimized prior any fertilisation event,
416 even in P deficient soils, as it influences the retention of applied P. Organic and residual P
417 pools were partially mineralized in most of the soils, indicating mobilisation towards more
418 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 dependant 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

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436

437

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622

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.

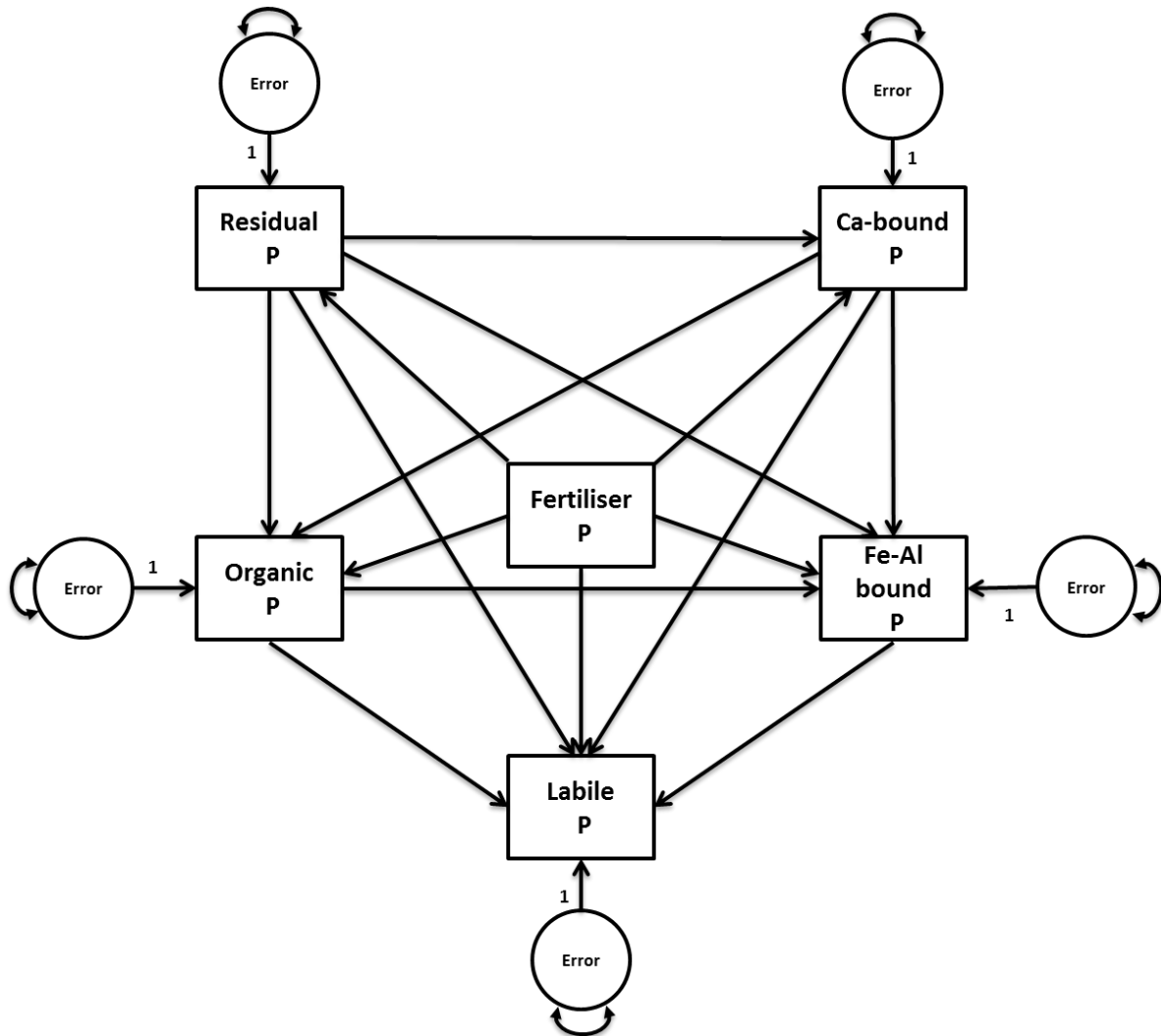
Soil property	Units	Galway peat	Galway peaty mineral	Cork mineral	Cork peaty mineral	Wexford mineral	Wexford peaty mineral
Classification*		Ombric Histosol	Haplic Cambisol	Haplic Stagnosol	Haplic Stagnosol	Haplic Cambisol	Haplic Podzol
Texture		Sandy Loam	Sandy Loam	Clay Loam	Sandy Clay Loam	Loam	Sandy 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
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)

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

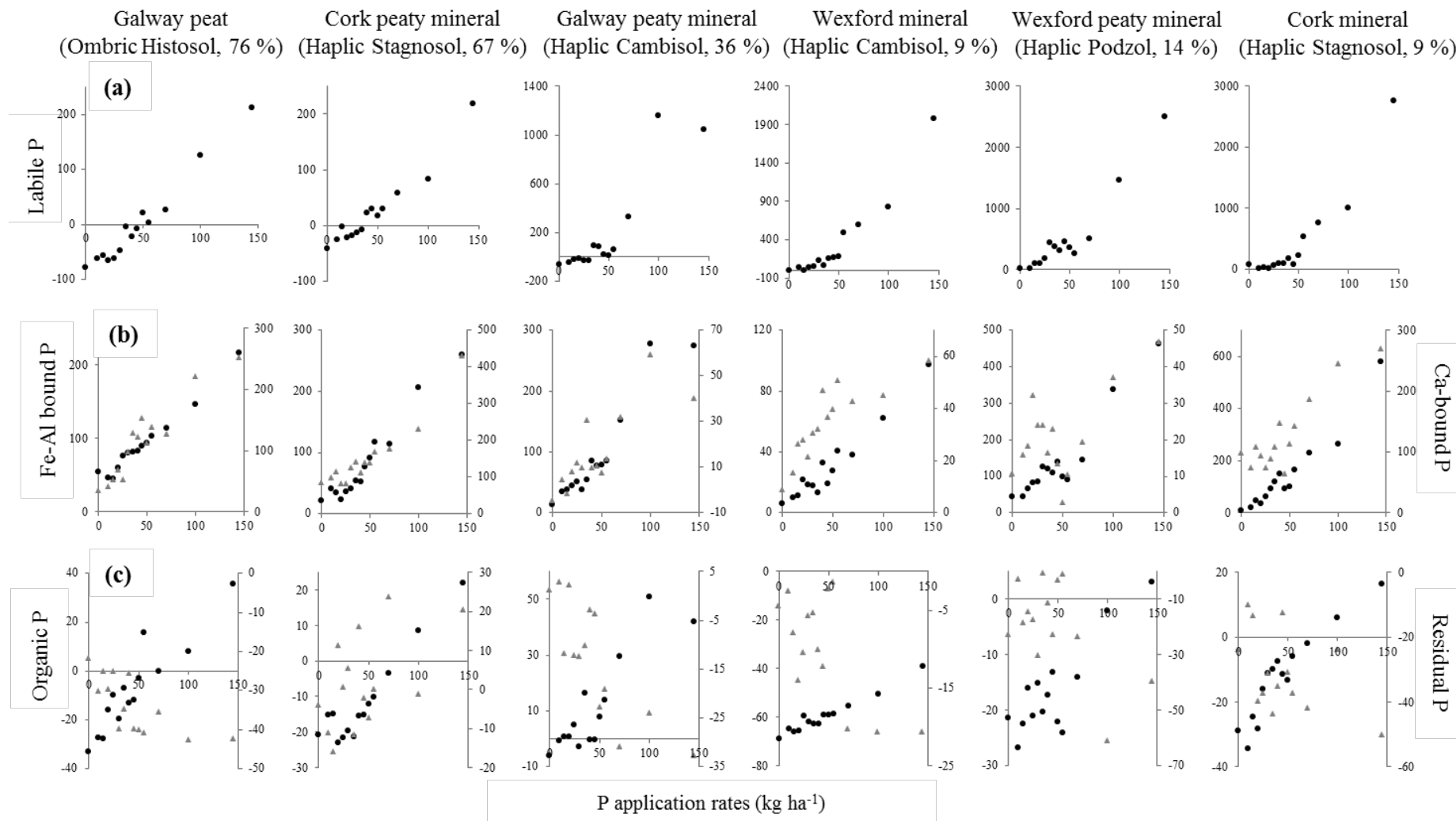
Table 2. Unstandardized partial regression coefficients. Direct (diagonal, bold) and indirect (off diagonal) contribution of P fertiliser applications on the different soil P pools. Significant levels at $p \leq 0.05$, 0.01 and 0.001 represented by *, ** and ***, respectively. NS = not significant.

Variable	Residual	Ca-bound P	Organic P	Fe-Al bound P	Labile P
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*

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, ● symbol) and Residual P (right vertical axis, ▲ symbol) fractions across P applications in
- 2 the six soils studied. Percentages represent the organic matter content.
- 3



5 **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.
 6 P Uptake was calculated by multiplying the cumulative grass dry matter yield at each P dose by the average herbage P content. The miniature
 7 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
 8 matter content.
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