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Phosphorus sorption, supply potential and availability in soils with contrasting parent material and soil chemical properties

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European Journal of Soil Science

DOI:
[10.1111/ejss.12260](https://doi.org/10.1111/ejss.12260)

Published: 01/07/2016

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):
Daly, K., Styles, D., Lalor, S., & Wall, D. P. (2016). Phosphorus sorption, supply potential and availability in soils with contrasting parent material and soil chemical properties. *European Journal of Soil Science*, 66(4), 792-801. <https://doi.org/10.1111/ejss.12260>

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1 **Phosphorus sorption, supply potential and availability in soils with**
2 **contrasting parent material and soil chemical properties.**

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14 *Running title: Phosphorus sorption and buffering*

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17 *Keywords: Phosphorus, desorption, phosphorus solubility, soil fertility, buffering capacity,*
18 *temperate soils.*

19

20

21 **Summary**

22

23 Soil phosphorus (P) management requires a more targeted and soil specific approach than is
24 currently applied for agronomic recommendations and environmental evaluation.
25 Phosphorus buffering capacities control the supply of P in the soil solution and were
26 measured across Irish soils with contrasting parent material and chemical properties.
27 Langmuir sorption buffer capacities (MBC) and binding energies (b) were strongly correlated
28 with soil pH and extractable aluminium (Al). A broken-line regression fitted to the
29 relationship between MBC and Al derived a change-point value for Al above which MBC
30 increased linearly. Soils above the change point were predominantly acidic to neutral with
31 non-calcareous parent material, larger buffering capacities and binding energies than
32 calcareous soils. Ratios of Mehlich3-Al and P (Al:P) were used to relate buffering capacity
33 with supply potential in non-calcareous soils. Large ratios of Al:P were associated with poor
34 P availability, characteristic of strongly P fixing soils. Threshold values of iron-oxide paper
35 strip P (FeO-P) and Morgan's P revealed Al:P ratios where soils began to supply P in
36 available form. The change-point for Morgan's P fell within the current target index for P
37 availability; however, the confidence interval was more compatible with previous agronomic
38 P indices used in Ireland. Relationships between Morgan's P and measures of extractable P,
39 M3-P and Olsen P, deviated in calcareous soils at large soil P contents, indicative of P
40 precipitation processes dominating in these soils. Identifying differences in soil P buffering
41 capacity at laboratory scale would improve agronomic and environmental assessment at field
42 and catchment scales.

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46 **Introduction**

47

48 Phosphorus (P) is an essential element to all known life and an adequate supply is required in
49 agricultural soils to meet the demands for crop growth and grazing animal health. The finite
50 nature of rock phosphate and Europe's dependence on imports from China and Asia and
51 North Africa, is putting its supply under pressure as reserves are diminishing (Cordell *et al.*
52 2009). The majority (79%) of the P imported is used to make fertilizer for use in agriculture
53 and food production and in animal feeds (11%) (Johnston & Steen, 2000). In many countries,
54 fertilizer P recommendations are based on P index systems where bands of soil test P values
55 are used to guide application rates. In Ireland the agronomic soil test for P is Morgan's
56 extractable P, and for easier management and knowledge transfer at the farm scale Morgan's
57 P levels have been categorized as indices; 1 (deficient), 2 (low), and 3 (agronomic optimum)
58 and 4 (excessive) (Lalor & Coulter, 2008). Fertilizer recommendations have been
59 inextricably linked with soil tests since the 1950s and 1960s, following the general
60 philosophy of 'build up and maintenance' (Vos, 1998). In recent years the agri-environmental
61 landscape has changed, especially, since the implementation of water quality directives.

62 . Morgan's P values are now used as the basis for risk assessment of P loss from Irish soils.
63 Going forward, farmers face huge challenges in managing P resources on farms including
64 increased P requirements for sustainable intensification to meet rising global food demands,
65 the maintenance of soil fertility under stringent environmental constraints and increasingly
66 expensive P fertiliser. The growing need for economic and environmental sustainability has
67 stimulated interest in efficient P fertilizer utilization and nutrient management on farms.

68 Future soil fertility management requires a more targeted and soil specific approach
69 than is currently applied, to maximize the crop use efficiency of valuable P inputs, and to
70 increase the P supplying capacities of soils under reduced P input regimes. Phosphorus

71 buffering capacity is described as the ability to supply soluble P as a function of capacity, and
72 differences in P buffering and sorption capacities can significantly influence supply and
73 availability of P in a water soluble form (Burkitt *et al.* 2001).

74 Whilst it has been accepted that no soil test is universal (Vos, 1998), recent research
75 incorporating P sorption and buffering with soil P tests, has provided P indices that are soil-
76 type specific for improved critical soil test P predictions to give a value of soil test P where
77 availability is optimized (Moody *et al.* 1997; Van Rotterdam *et al.* 2010). Similarly,
78 quality/intensity relationships have provided useful indices for predicting supply of slowly
79 available P in soils using easily measured soil properties with traditional soil tests (McLaren
80 *et al.* 2014; Van Rotterdam *et al.* 2012). More recently, Reijneveld *et al.* (2014) proposed a
81 strategy for modelling novel methods of P capacity and intensity, with historical P tests,
82 combined with field trials, for agronomic recommendations and environmental evaluations.

83 Over the past decade Irish fertiliser P recommendations have been updated for
84 grassland soils in Ireland, using results from a fertilizer response trial that did not
85 differentiate soil type, (Schulte & Herlihy, 2007). The objectives of this present study were to
86 measure P buffering capacities across a range of Irish grassland soils with contrasting parent
87 material and chemical properties and relate these values to soil attributes, pertaining to P
88 availability and supply. Soil samples with contrasting parent material and chemistry were
89 collected from grassland sites across Ireland and the relevance of contrasting soil P buffering
90 and sorption is discussed with regard to availability and examined in the context of our
91 current revised agronomic recommendations.

92

93

94

95

96 **Materials and methods**

97

98 *Soil Sampling*

99 Principal agricultural soils were identified from the General Soil Map of Ireland (Gardiner &
100 Radford, 1980), the mapping unit of which is the soil association. These include
101 amalgamations of Great Soil Groups and associated parent material, and for this study, 120
102 sampling locations were identified that best represented principal soil associations used in
103 grassland systems in Ireland (Table 1). The soil sampling programme also targeted sites with
104 a range of soil test P levels (Morgan's P) so that the agronomic P indices were reflected in the
105 data. Samples were taken on field-by-field basis to a depth of 100 mm with a soil corer (1.5-
106 cm diameter) with approximately 30–40 cores bulked to provide a composite sample from
107 each field and prior to the spreading of fertilizers and manures. One hundred and twenty
108 samples were air-dried and sieved to remove roots and stones (2 mm mesh) and stored in air-
109 tight boxes at room temperature prior to analysis.

110

111 *Phosphorus sorption isotherms*

112 Phosphorus sorption isotherms were derived using a modification of the standardized batch
113 technique by Nair *et al.* (1984). Because of the time consuming nature of this technique, a
114 sub-set of 74 soil samples, representing each soil association, were equilibrated with P in
115 solution and the data was evaluated using the Langmuir model (Paulter & Sims, 2000) as
116 follows. Six, 40-ml solutions of P concentration 0, 5, 10, 15, 20 and 25 mg l⁻¹ in KH₂PO₄
117 were added to 2 g soil samples in 50ml centrifuge tubes in duplicate. The suspensions were
118 shaken at room temperature for 24 hour, centrifuged and filtered, and the concentration of P
119 in solution was measured colorimetrically (John, 1970) using the molybdate blue method.
120 Phosphorus sorbed to the soil was calculated as the difference between initial concentration

121 and P concentration measured at equilibrium. Adsorption data and affinity constants were
122 determined by fitting sorption data to the Langmuir isotherm equation:

$$123 \quad C/X = 1/X_m \times b + C/X_m, \quad (1)$$

124 which represents a straight line where X is P sorbed (mg P kg^{-1}), C is the equilibrium P
125 concentration (mg P l^{-1}) with an intercept $1/X_m \times b$ and slope $1/X_m$. The linear form of the
126 Langmuir equation was then used to derive X_m , the sorption maximum (mg P kg^{-1}) and b, a
127 constant related to the binding energy (l mg^{-1}). Phosphorus sorption isotherms were plotted
128 for each soil sample collected and the Langmuir model derived sorption maximum (X_m , mg
129 kg^{-1}), binding energy (b, l mg^{-1}). Maximum buffer capacity (MBC, l kg^{-1}) was calculated as
130 the product of X_m and b (Indiati *et al.* 1999).

131

132 *Extractable P (FeO-P, Olsen P, Mehlich3-P, Morgan's P)*

133 The iron-oxide paper strip test was used as a P sink method for estimating labile inorganic P
134 on 120 soils sampled, according to the method of Menon *et al.* (1988). One FeO-impregnated
135 paper strip (100 x 20 mm) was added to each sample of soil (1 g) suspended in 40 ml of 0.01
136 M CaCl_2 solution and shaken for 16 hour on an end-over-end shaker. The paper strips were
137 eluted with 40 ml 0.1 M H_2SO_4 for one hour and the P concentrations in the acidic solution
138 determined colorimetrically. Morgan's P was determined on 120 soils, with 6.5 ml of soil in a
139 buffered acetate-acetic acid reagent at a 1:5 (v/v) soil to solution ratio extracting for 30
140 minutes (Peech & English, 1944). Mehlich3-P (M3-P) was determined on 120 soils using the
141 modified Mehlich test (Mehlich, 1984) to extract P, aluminium (Al), iron (Fe) and calcium
142 (Ca), at a 1:10 soil solution ratio of 2 g of soil shaken with 20 ml Mehlich3 reagent (0.2 M
143 $\text{CH}_3\text{COOH} + 0.25 \text{ M NH}_4\text{NO}_3 + 0.015 \text{ M NH}_4\text{F} + 0.13\text{M HNO}_3 + 0.001\text{M EDTA}$) for 5
144 minutes on a reciprocating shaker. The extracts were filtered and P in solution measured
145 colorimetrically with a molybdate blue method (John, 1970). Olsen P was measured on 60

146 samples only because of a lack of sample availability. This method used 2-g sample shaken
147 with 40 ml 0.5 M NaHCO₃, buffered at pH 8.5, for 30 minutes. Phosphorus concentration in
148 the solution was determined colorimetrically with a molybdate blue method (John, 1970).

149 Soil pH was determined on a 2:1 soil-water ratio paste on 120 samples and percentage
150 organic matter (% OM) measured from 120 samples as the loss-on-ignition of 5-g samples at
151 500° C. Results were analysed with SAS Enterprise Guide V5 to obtain correlation and
152 regression information. The NLMIXED procedure in SAS was used for change-point
153 analysis and broken-line regression. Optimization was performed using the dual quasi-
154 Newton algorithm, with a dual Broyden, Fletcher, Goldfarb, and Shanno (BFGS) update of
155 the Cholesky factor of an approximate Hessian. PROC NLMIXED computes approximate
156 standard errors for estimates and predictions using the delta method of truncated expansions.

157

158 **Results**

159

160 *Chemical properties of soils collected*

161 Soil chemical properties of representative soil associations are presented in Table 2 and their
162 correlations are tabulated in Table 3. Soil pH ranged from 4.7–7.1, with smallest values
163 measured in soil associations 14, 15 and 25 and largest values recorded in soil associations 30
164 and 34 on limestone parent material. Extractable Ca, ranged from 284-8660 mg kg⁻¹ across
165 all soils and was positively correlated with soil pH ($r = 0.80$). Extractable Al and Fe ranged
166 from 69-1730 mg kg⁻¹ and 215-666 mg kg⁻¹, respectively with largest concentrations
167 measured on soil associations 14 and 25. Extractable Al was negatively correlated with soil
168 pH ($r = -0.71$) and largest concentrations associated with acidic soils. Across all soil
169 associations, OM% ranged from 5.3–15.7 % and some weak but significant correlations were
170 observed between OM% and extractable Fe ($r = 0.47$) and Ca ($r = 0.32$) possibly indicating

171 the presence of amorphous forms of Fe and Ca among these soils. Morgan's P ranged from
172 1.5–32.9 mg l⁻¹ and correlated with other P extraction methods, where the strongest
173 correlations were observed with M3-P ($r = 0.79$) and FeO-P ($r = 0.73$) and weakest with
174 Olsen-P ($r = 0.63$). Across all soils, Mehlich3 extracted of the most P (13.4–285 mg kg⁻¹),
175 followed by FeO-P (15.4–128 mg kg⁻¹) and Olsen-P (8.9–89.6 mg kg⁻¹).

176

177 *Langmuir sorption properties*

178 The Langmuir model provided a highly significant ($P < 0.001$) fit to soils in this study ($R^2 >$
179 0.95) and values of Langmuir parameters X_m , b and MBC derived from the isotherms across
180 all soil associations are presented in Table 2. Soil pH was inversely correlated with all of the
181 Langmuir sorption parameters X_m , ($r = -0.46$), b ($r = -0.62$) and MBC ($r = -0.65$) whilst
182 extractable Al positively correlated with X_m , b and MBC. These soil attributes provided the
183 strongest correlations with Langmuir sorption terms, although the scatter plots were
184 nonlinear. Soil pH accounted for 55% of the variation in log transformed MBC (Figure 1)
185 with buffering capacity decreasing as soil pH increased from 4.7 to 7.1. The regression
186 equation is listed in Table 4. Soil associations derived from limestone parent material
187 recorded the smallest values of each of the Langmuir terms with typically high pH values of
188 >6.0 . Visual inspection of the relationship between MBC and Al indicated small MBC
189 values at small Al values with a sharp increase in MBC above a threshold Al value. This
190 threshold value was derived by regression modelling of the data where a broken-line
191 regression was fitted to log transformed MBC and extractable Al in Figure 2, and a
192 significant change-point ($P < 0.001$) derived at an Al concentration of 612 (+/- 104) mg kg⁻¹,
193 above which buffer capacity in soil increased linearly with increasing Al. Parameter estimates
194 for this relationship are presented in Table 5. Above the upper confidence limit of the
195 change-point for Al (>716 mg kg⁻¹), soils was predominantly derived from non-calcareous

196 parent material. This group of soils were characterised by predominantly low pH values
197 ranging from 4.7 to 6.3 (mean = 5.3) and strong Langmuir sorption properties. Mean MBC
198 and b values in these soils were 1250 l kg^{-1} and 2.56 l mg^{-1} , respectively, and mean Al and Ca
199 values of 1072 and 1451 mg kg^{-1} , respectively. These soils are denoted here as non-
200 calcareous soils ($n = 76$) and their summary statistics are presented in Table 6. When
201 separated out from the overall data, Al in these soils accounted for 65% and 57% of the
202 variation in MBC and b, respectively. The remaining soils, were mostly soil associations
203 derived from limestone parent material, with soil pH in the range 5.2–7.1, mean extractable
204 Ca values of 3487 mg kg^{-1} , and mean MBC and b values of 346 l kg^{-1} and 1.01 l mg^{-1} ,
205 respectively. These soils are denoted here as calcareous ($n = 44$). There were no significant
206 correlations between Al, Ca and Fe and any of the Langmuir sorption values in the calcareous
207 soils group. Four samples with Al values of (776–779 mg kg^{-1}) that exceeded the upper value
208 of the 95% confidence interval around the change-point were assigned to the calcareous
209 group because of parent material, large Ca values and weak Langmuir sorption properties.

210

211 *Aluminium to phosphorus ratios in non-calcareous soils.*

212 There was no direct correlation between the Langmuir terms and the different measures of
213 extractable P, except for a weak correlation between X_m and FeO-P ($r = 0.26$). Given that
214 buffering capacity and affinity in non-calcareous soils was strongly associated with
215 extractable Al, the ratio of M3-Al and M3-P (Al:P) was used to infer sorptive capacity and
216 ability to supply P, in these soils. This ratio describes capacity and affinity for P, relative to P
217 already sorbed. The weight ratios developed for Al:P were in line with other studies using
218 Ca:P ratios (McLaren *et al.* 2014) with practical significance since soil testing laboratories
219 tend to record results on a weight basis. To relate P buffering to supply in soluble and plant
220 available forms, ratios of Al:P were plotted against P desorption and availability as measured

221 by FeO-P and Morgan's P and the relationship is depicted in Figures 3(a). The smallest FeO-
222 P values corresponded to large Al:P ratios, however, as Al:P ratios decreased towards a point
223 of inflection on the graph, below which, FeO-P increased steadily. Following the pattern in
224 the data, a broken line regression was fitted and a significant change-point was found (P
225 <0.001) at the FeO-P value of 43.2 mg kg^{-1} within a lower and upper 95% confidence interval
226 of 32.3 and 53.9 mg kg^{-1} , respectively. The value of Al:P at this change-point was 8.1 within
227 a confidence interval of 5.5 and 11.8 , respectively. To relate buffering to agronomic P, the
228 relationship between Al:P and Morgan's P was examined and a significant change-point was
229 found in the relationship ($P < 0.001$). A broken line regression fitted to the data derived a
230 change-point for Morgan's P at 7.3 mg l^{-1} within a 95% confidence interval of 5.9 and 8.7 mg
231 l^{-1} (Figure 3(b)). The value of Al:P at the Morgan's P change-point was 11.7 within the
232 confidence interval of 9.2 and 15.0 . Since the estimate of 11.7 for Al:P at the Morgan's P
233 change-point falls within the confidence interval for value of Al:P at the FeO-P change-point,
234 they are not significantly different. Thus the Al:P ratio at the Morgan's P change-point is
235 consistent, within the range of possible values estimated at the FeO-P change-point. The
236 parameter estimates for relationships in Figure 3(a) and 3(b) are presented in Table 5.

237

238 *Calcium to P ratios in calcareous soils*

239 Mehlich3 extractable Ca and P were expressed as a ratio (Ca:P) and plotted against values of
240 FeO-P and Morgan's P in a similar analysis for calcareous soils. One sample with an
241 extremely large Ca value of 8888 mg kg^{-1} which biased the relationship was removed from
242 the analysis and a non-linear, negative relationship between Ca:P and FeO-P ($R^2 = 0.32$) and
243 Morgan's P ($R^2 = 0.33$), was observed. These relationships showed no change points above
244 or below which, P became more or less available, and the regressions were not strong enough
245 to be predictive.

246

247 *Relationship between P tests in calcareous and non-calcareous soils.*

248 The standard agronomic P test used in Ireland, Morgan's P, was significantly correlated with
249 each of the other extractable P methods FeO-P ($r = 0.73$), M3-P ($r = 0.79$) and Olsen-P ($r =$
250 0.63) across all soils. Correlations across all soils may conceal the effect that variations in Al
251 and Ca could have on extraction efficiency in the soils presented in this study. Figures 4(a)
252 and 4(b) depict the relationship between Morgan's P and measures of available P M3-P,
253 Olsen-P, for non-calcareous and calcareous soil groups. The relationships between Morgan's
254 P and M3-P, and Olsen P were broadly similar within each of the soil group, however, they
255 deviated as soil P concentrations increased, indicating less extractable M3-P and Olsen-P at a
256 given Morgan's P concentration in the calcareous soils. The relationship between FeO-P and
257 Morgan's P (Figure 5) was more comparable between soil groups within the typical
258 agronomic range (Morgan's P 0–10 mg l⁻¹) but had some divergence in the relationship at
259 very large P values. However, only a small number of samples were present at extremely
260 large Morgan's P values. Overall, the relationships between these variables was stronger in
261 non-calcareous ($R^2 = 0.71$) compared to calcareous soils ($R^2 = 0.42$) and the regression
262 equations between soil tests are presented in Table 4.

263

264 **Discussion**

265

266 *Langmuir sorption properties and soil characteristics*

267 Values of Langmuir sorption parameters in this present study are in line with those reported
268 elsewhere on agricultural soils over a soil pH range 4.6–8.3 (Indiati *et al.* 1999). These
269 authors reported X_m ranging from 37.2–4990 mg kg⁻¹, b values from 0.75–6.12 l mg⁻¹ and
270 MBC values from 51.4–5260.8 l kg⁻¹. Quintero *et al.* (1999) reported a decrease in P

271 retention and maximum buffering capacities in soils as pH increased from 3 to 7, and
272 attributed a strong buffering capacity to large amounts of both Al and Fe, in line with results
273 reported here. Calcareous soils in this present study recorded small values of X_m , b and MBC
274 and which are in line with those reported by Amrani *et al.* (1999) on calcareous soils in
275 Manitoba with Langmuir buffer capacities and affinity values between 146 – 808 l kg⁻¹ and
276 0.15 - 0.6 l mg⁻¹, respectively.

277 Soils grouped as non-calcareous exhibited greater X_m , b and MBC, because of their
278 greater amounts of extractable Al. Broggi *et al.* (2011) found significant influence of soil pH
279 and Al content, with smaller adsorption energies in limed soils. In this present study, soil pH
280 and Al were negatively correlated with each other and associated with strong P sorbing soils.
281 The strong association between P sorption and amounts of extractable Al in preference to Fe
282 is also in line with other international, (Burkitt *et al.* 2002; Paulter and Sims, 2000) and Irish
283 studies (Daly *et al.* 2001; Maguire *et al.* 2001). Consistent with results reported here, some
284 researchers reported Al to be more strongly correlated than Fe with P sorption (Villapando &
285 Graetz, 2001). Extractable Al is also strongly associated with plant growth and Ballard &
286 Fiskell (1974) concluded that the dominant nature of extractable Al provides the best
287 indicator of P retention in soils.

288

289 *Relating sorptive properties to P supply*

290 To relate measures of extractable P to sorptive properties, the relationship between ratios of
291 M3 extractable Al:P and FeO-P was described by a broken-line regression with change-
292 points which revealed a value for Al:P below which FeO-P concentrations increased steadily.
293 Above this Al:P change-point, soils were characterized as strongly P sorbing, indicative of
294 poor Al-P solubility. A similar relationship was found between Al:P and Morgan's P and the
295 change point corresponded to a Morgan's P value of 7.3 mg l⁻¹. This value falls within the

296 upper end of the current soil test P index range for optimum P availability ($5.1\text{--}8\text{ mg l}^{-1}$) set
297 for Irish soils by Schulte & Herlihy (2007). Above the Al:P change-points for both FeO-P
298 and Morgan's P it is likely that the P sorbed on surface oxides of Al was more tightly sorbed
299 and less available for release as soluble and plant available forms. Once the amounts of P
300 increased in the soils and reduced the Al:P ratios below the change point values, the soils
301 began to supply P in soluble and plant-available forms. The Al:P values at the change-points
302 for both FeO-P and Morgan's P were consistent and not statistically different. Soils below the
303 change-point were typified by large MBC and b values, with low pH and large Al
304 concentrations and are described here as strong 'P fixing' non-calcareous soils. Quintero *et*
305 *al.* (1999) reported that 70 % of added P in strongly P fixing soils remained in the non-labile
306 P pools, whereas 30–40 % of P added to soils with poor buffering capacity was non-labile,
307 and noted that greater rates of fertilizer P are required for soils with large Al and Fe contents
308 to reach an optimum P availability for plant uptake. Similarly, Fernandez & Warren (1994)
309 related different sorption properties to varying amounts of extractable Al and concluded that
310 fertiliser rates should vary according to amount of Al in soils. Our results implications for
311 fertilizer recommendations on strong P fixing soils where Al:P ratios are large although
312 require further data to be able to revise existing recommendations. However, this work
313 provides easily measured soil properties (Al:P) that can be combined with conventional soil
314 testing to describe P supply potential across soils with different sorptive properties.

315

316 *Interpreting the Morgan's P threshold within agronomic P indices.*

317 Across the soils studied here the change-point value for Morgan's P of 7.3 mg l^{-1} in Figure
318 3(b) represents the ability to supply P in a plant available form consistently. Accounting for
319 some of the variability between soils a confidence interval around this change-point
320 Morgan's P concentration of $5.9\text{ to }8.7\text{ mg l}^{-1}$ was calculated. This range is possibly more

321 compatible with the previous target index (Index 3) range of 6.1 to 10 mg l⁻¹ Morgan's P
322 (Coulter, 2004), before they were revised downward to 5.1–8 mg l⁻¹. These revised values
323 were based on grass yield response studies of a range of fertilizer P inputs over 8 soil series
324 (Schulte & Herlihy, 2007). However, the soils used in the latter trial comprised of four
325 limestone and four non-limestone parent material soil groups, and did not cover the range of
326 soil chemistry found in soils in Ireland. The fertilizer rates required to reach 95% potential
327 yield and herbage P concentration of 3.0 g kg⁻¹ were not statistically related to differences
328 between soil types or parent material groups. The lack of contrast in soil chemical properties
329 across the eight soil series failed to provide the statistical significance required to include soil
330 type as a factor and ultimately resulted in a P index system that does not account for
331 differences in P sorption or buffering capacities that could influence fertilizer uptake and
332 critical soil P values.

333 The difference in P sorption characteristics between calcareous and non-calcareous
334 soils in this present study results largely from contrasting soil properties such as soil pH and
335 extractable Al and Ca. Herlihy & McGrath (2007) found no significant difference in
336 Langmuir sorption maxima among soil series and soil parent material groups (limestone
337 verses non-limestone) with the exception of equilibrium buffer capacity (EBC) values for the
338 range 0-3 mg l⁻¹ P where there were larger values were observed in the non-limestone soil
339 groups. They also reported no significant differences in pH, clay, oxalate-extractable Al, with
340 the exception of significantly larger oxalate extractable Fe in non-limestone soils. The lack of
341 contrast between their soil groups in terms of chemical properties made it difficult to
342 statistically distinguish sorption characteristics in their data.

343

344 *Processes of sorption and precipitation: implications for soil P management*

345 In line with previous studies on Irish soils, extractable inorganic P as measured by M3-P,
346 Olsen-P and FeO-P were strongly correlated with Morgan's P on soils collected in this study
347 (Daly *et al.* 2001; Daly & Casey, 2005; Herlihy *et al.* 2006). However, the contrast in soils,
348 exhibited by differences in Langmuir sorption properties, soil pH and amounts of extractable
349 Al, Fe and Ca, influenced the relationships between extractable P and Morgan's P. These
350 relationships indicated larger Olsen and M3-P concentrations in non-calcareous soils and
351 smaller concentrations in calcareous soils, at similar Morgan's P values, particularly as soil
352 test P concentrations increased. The relationship between Olsen-P and Morgan's P was
353 reported for 199 soils sampled in the cross-border region of Northern Ireland (Foy *et al.*
354 1997) and although the soil tests were strongly related ($R^2=0.70$), the authors reported the
355 Olsen-Morgan relationship in high pH soils and soils over carboniferous geology followed a
356 different trend in predicting the smallest Olsen-P values. The relationship between Morgan's
357 P and Olsen-P in this present study concurs with Foy *et al.* (1997) with the smallest Olsen-P
358 values observed in the calcareous soils at similar Morgan's P values. Morgan's P may be
359 over-estimating Olsen-P and M3-P at large P values P in calcareous soils, where the process
360 of Ca-P precipitation becomes dominant at large soil P contents.

361 The FeO-P values were more comparable in non-calcareous and calcareous soil
362 groups at similar Morgan's P value and the relationship showed only slight divergence at
363 greater extremes of soil test P concentrations. The FeO-P test is reported to be a 'P sink'
364 method, favoured over chemical extraction for estimates of P desorption and for quantity
365 intensity relationships, as it is not confounded by chemistry (McLaren *et al.* 2014; Van
366 Rotterdam *et al.* 2012) and suitable across soil types.

367 These diverging relationships indicate stronger sorptive properties in highly buffered
368 soils (Dougherty *et al.* 2011) with a larger pool of P in non-calcareous soils that can
369 continuously supply P to the soil solution and precipitation of Ca-P at large P values in

370 calcareous soils. Chemical fractionation on calcareous soils has recorded 98% of total
371 inorganic P as Ca-P and desorption from the soil matrix using FeO strips was related to labile
372 P available for plant uptake (Ahmad *et al.* 2006). The interaction of P with soil components
373 in calcareous soils is controlled by both surface reactions and precipitation and at small P
374 concentrations non-carbonate clays provide surfaces for P adsorption. However, once these
375 sites have been filled, and at greater soil P concentrations, calcium carbonate plays a role in
376 the precipitation of P and subsequent reduction of P availability to the plant and soil solution
377 (Von Wandruszka, 2006).

378 Precipitation of Ca-P in soils at large P values could have implications for P transport
379 at the catchment scale. Mellander *et al.* (2012) recorded sub-hourly P concentrations and
380 discharge delivered to spring water in a karst catchment in western Ireland characterized by
381 calcareous parent material overlain by shallow soils. Despite a large proportion of soils
382 measuring excessive Morgan's P concentrations with a good connectivity to groundwater,
383 background P concentrations in groundwater were small and posed a low risk of increasing
384 surface water P concentrations. The authors conclude that processes of P attenuation in the
385 soil, geology and hydrology in this catchment were limiting P transfers to surface waters.
386 Smaller values of M3-P at large Morgan's P values in the calcareous soils in our study
387 supports the attenuation hypothesis in Mellander *et al.* (2012) that the process of desorption is
388 overtaken by precipitation at elevated soil P contents.

389 Herlihy *et al.* (2004) reported results from a P trial that included a 'zero P treatment'
390 on soils across the full range of soil P indices (1–4) used in Ireland, for both calcareous and
391 non-calcareous soil parent material groups. They reported more rapid rates of decline in soil
392 test P in limestone soils at low P indices that could possibly be explained by the poorer
393 buffering in these soils compared to the non-limestone soil group. As P is depleted from the
394 soil solution phase from plant uptake and not replaced in added fertilizer, soils that are better

395 buffered can utilise their larger store of labile inorganic P reserves to replenish the soil
396 solution phase more rapidly than poorly buffered soils with smaller overall P reserves which
397 may be more tightly held in the shorter term. Strongly buffered soil will exhibit a slower rate
398 of decline in soil test P concentration than poorly buffered soils over time and modelling
399 studies on Irish soils (Schulte *et al.* 2010) could consider including sorptive properties such
400 as Al:P to improve estimates.

401 Differences in soil P supply and release between calcareous and non-calcareous soils
402 have implications for how P fertilizer application should be managed. For non-calcareous
403 soils splitting the annual P allowance using a little and often approach to P application for
404 grassland, over the annual growing season may be more appropriate for maintaining adequate
405 P in soil solution for soils with P concentrations below the change-point for Morgan's P (<
406 7.3 mg l⁻¹) with Al:P ratios above those at the change-point. Above the threshold Morgan's P
407 value, maintenance P applications could be applied at the start of the growing season. In
408 contrast it may be less important to split the annual P application for calcareous soils as a
409 smaller proportion of added P would be fixed. In terms of P build-up, calcareous soils may
410 require less P fertilizer overall than strong high P fixing soils to build up to the agronomic
411 optimal range (Index 3) because the binding energies are less in these soils.

412

413 **Conclusions and Recommendations**

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415 Phosphorus dynamics in grassland soils are controlled by the chemical nature of the soil and
416 the P retained in soil. In this study, P sorptive capacity and strength to which P is bound in
417 soil was to a large extent influenced by soil pH and amounts of extractable Al. This was
418 illustrated by a change-point value of extractable Al in soil, above which P buffering
419 capacities increased linearly, facilitating the classification of soils into calcareous and non-

420 calcareous groups. Non-calcareous soils with large buffering capacities had larger P reserves
421 at similar soil test P than calcareous soils with smaller P buffer capacities. Acknowledging
422 differences in P buffering capacities in grassland soils, combined with soil P testing, could
423 improve P management and efficiency; however, sorption isotherms are too time consuming
424 for routine soil testing. Ratios of Al:P could be used as a surrogate for Langmuir buffer
425 capacities in non-calcareous soils, as this indicator was related to supply potential and release
426 of P in an available form. This indicates the potential for incorporating easily measured soil
427 chemical properties with agronomic P testing, particularly for strong P fixing soils where P
428 availability could be improved by adjusting Al:P ratios. Diverging relationships between soil
429 P tests in calcareous and non-calcareous soils can be attributed to differences in P reserves in
430 strongly buffered non-calcareous soils, and P precipitation at large P contents, in calcareous
431 soils with poor P buffering capacities. Distinguishing differences in P buffering in soil, at
432 process scale, will support improved agronomic and environmental assessment at both field
433 and catchment scale, specifically, our interpretation of P build up and release, P balances,
434 rates of soil P decline and P attenuation in catchments.

435

436 **Acknowledgement**

437

438 The authors would like to thank Dr. Jim Grant for statistical advice and support and his
439 technical assistance in data analysis.

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Table 1 The locations and description of soil associations used for sample collection, describing arrangements of Great Soil Groups and associated parent material with texture and drainage class included (Gardiner & Radford, 1980).

Location	Soil Association	Great Soil Groups	Parent Material	Texture class	Drainage class
Tipperary	34	Luvisol (70%), Gleysol (20%), Cambisol (10%)	Gravelly limestone till	Gravelly loam	Well drained
Tipperary	30	Luvisol (70%), Cambisol (20%), Gleysol (5%), Histosol (5%).	Calcareous, limestone till	Sandy loam	Well drained
Cork	15	Podzol (60%), Cambisol (20%), Gleysol (20%)	Old red sandstone, shale	Gravelly loam	Well drained
Roscommon	31	Luvisol (80%), Gleysol (10%), Cambisol (5%), Histosol (5%).	Calcareous glacial till	Loam	Well drained
Tyrone	25	Gleysol (50%), Cambisol (40%), Histosol (10%)	Silurian sandstone-shale composition	Clay loam	Imperfect to poor
Meath	14	Cambisol (75%), Gleysol (15%), Podzol (10%)	Ordovician shale, glacial till.	Loam	Well drained

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Table 2. Range (min-max) of soil properties measured across samples collected from soil association listed in Table 1. Soil pH, %Organic matter (% OM), Morgan's P, Iron-oxide paper-strip P (FeO-P), Mehlich3 extractable Al, Fe, Ca and P (M3-P) were measured on all soils (n = 120). Across soil associations Langmuir sorption isotherm values were derived for a subset of samples (n = 74). Olsen extractable P (Olsen-P) derived for a sub-set of soils (n = 60) did not include soil associations 30 and 14.

Soil Associatio n	pH	OM / %	Al	Fe	Ca	Xm	Langmuir Terms		Morgan's P / mg l ⁻¹	Phosphorus Extracts		
							b / l mg ⁻¹	MBC / l kg ⁻¹		M3-P	FeO-P	Olsen-P
34	5.2-7.0	5.7-15.4	69-1160	215-642	1420-8660	263-333	0.66-4.48	213-476	1.5-32.9	18-168	21.6-38	14.6-57.6
30	5.4-7.1	5.5-11.9	349-780	254-592	1795-5543	263-400	0.63-1.29	250-417	1.6-17.5	17.8-101	19.6-69.6	
15	5.0-6.7	8.3-15.7	580-1530	454-655	894-5674	270-625	0.54-2.71	147-1429	6.6-18.2	60.8-211	39.8-83.2	30.6-77.5
31	4.9-6.9	5.9-15.5	317-1240	306-612	777-5040	303-435	0.35-2.0	119-769	1.5-11.8	13.4-110	15.4-58.4	8.9-34.2
25	4.8-6.3	5.3-14.5	901-1730	390-666	284-3566	385-588	1.43-7.67	714-3333	1.8-25.8	18.4-285	15.4-128	15.5-89.6
14	4.7-6.4	7.5-14.7	254-1730	373-556	769-4721	357-556	1.0-2.89	435-1429	2.6-9.2	30.5-114	17.4-59.2	

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Table 3. Pearson product moment correlation matrix of r-values significant at $P = 0.05$ derived between soil pH, % organic matter (OM), Mehlich3 extractable P, Al, Fe and Ca / mg kg⁻¹, Morgan's P / mg l⁻¹, Olsen-P / mg kg⁻¹ and iron-oxide paper strip P (FeO-P / mg kg⁻¹). Sorption properties include Langmuir sorption maximum (Xm / mg kg⁻¹); binding energy, (b / l mg⁻¹) and maximum buffer capacity, (MBC / 1 kg⁻¹). NS denotes non-significant correlation at $P = 0.05$.

	Xm	B	MBC	Morgan's P	M3-P	FeO-P	Olsen-P	pH	OM	Al	Fe	Ca
Xm	1.00											
b	0.38	1.00										
MBC	0.53	0.98	1.00									
Morgan's P	NS	NS	NS	1.00								
M3-P	0.41	NS	NS	0.79	1.00							
FeO-P	0.26	NS	NS	0.73	0.78	1.00						
Olsen-P	NS	NS	NS	0.63	0.88	0.78	1.00					
pH	-0.46	-0.62	-0.65	0.23	NS	NS	NS	1.00				
OM	0.29	NS	NS	0.31	0.37	0.23	0.42	NS	1.00			
Al	0.53	0.76	0.80	NS	0.22	NS	NS	-0.71	NS	1.00		
Fe	0.48	0.41	0.48	NS	0.40	NS	0.43	-0.48	0.47	0.55	1.00	
Ca	NS	-0.57	-0.58	0.24	NS	NS	NS	0.80	0.32	-0.66	-0.40	1.00

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Table 4 Regression equations for relationships between logMBC and soil pH across all soils, and relationships between Morgan's P and extractable measures of soil P, namely, Mehlich3-P, Olsen-P and iron-oxide paper strip P (FeO-P) for both calcareous and non-calcareous soils.

y	Equation		Coefficients	Standard errors	R ²
logMBC	y = a + (b x pH)	a	4.92	0.23	0.55
		b	-0.37	0.04	
M3-P non-calcareous soils	y = a + (b x Morgan's P)	a	8.14	5.59	0.83
		b	11.01	0.58	
M3-P calcareous soil	y = a + (b x Morgan's P)	a	22.47	4.35	0.80
		b	4.67	0.38	
Olsen-P non-calcareous soils	y = a + (b x Morgan's P)	a	9.34	3.82	0.66
		b	3.52	0.38	
Olsen-P calcareous soils	y = a + (b x Morgan's P)	a	15.64	4.19	0.62
		b	1.18	0.27	
FeO-P non-calcareous soils	y = a + (b x Morgan's P)	a	5.18	2.59	0.71
		b	3.68	0.27	
FeO-P calcareous soils	y = a + (b x Morgan's P)	a	21.68	3.00	0.42
		b	1.39	0.26	

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Table 5 Parameter estimates derived from the broken-line regressions fitted to non-calcareous soil data with change-points ($x = c$) highlighted in bold, for extractable Al mg kg⁻¹, FeO-P mg kg⁻¹ and Morgan's P mg l⁻¹.

		Estimate	Standard error	t value	<i>P</i>	95% confidence limit	
						Lower	Upper
Figure 2 (n = 73)	Intercept 1	6.1799	0.3299	18.73	<0.0001	5.5217	6.8381
	Slope 1	-0.0008	0.0007	-1.22	0.2280	-0.0023	0.0005
	x = c	611.92	52.1751	11.76	<0.0001	507.83	716.01
	Value of logMBC at change-point	5.6331	0.1324	42.54	<0.0001	5.3690	5.8973
	Slope 2	0.0029	0.0002	13.08	<0.0001	0.0024	0.0033
Figure 3(a) (n = 76)	Intercept 1	3.9422	0.1433	27.51	<0.0001	3.6568	4.2276
	Slope 1	-0.0402	0.0054	-7.40	<0.0001	-0.0511	-0.0294
	x = c	43.1187	5.4313	7.94	<0.0001	32.3013	53.9361
	Value of logAl:P at change-point	2.2048	0.1692	13.03	<0.0001	1.8678	2.5417
	Slope 2	-0.00861	0.004052	-2.12	0.0369	-0.1668	-0.0005
Figure 3(b) (n = 76)	Intercept 1	4.2247	0.1627	25.92	<0.0001	3.9006	4.5487
	Slope 1	-0.2297	0.0311	-7.37	<0.0001	-0.2917	-0.1676
	x = c	7.3041	0.7153	10.21	<0.0001	5.8794	8.7287
	Value of logAl:P at change-point	2.5471	0.1148	22.19	<0.0001	2.3185	2.7756
	Slope 2	-0.06198	0.01129	-5.49	<0.0001	-0.0844	-0.0395

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612 **Table 6** Summary statistics of general soil properties; pH, % organic matter (OM), Mehlich3 extractable Al, Fe, Ca, P, Morgan's P and iron-
 613 oxide paper strip P (FeO-P) of soils divided into non-calcareous (n = 76) and calcareous (n = 44) soil groups. Langmuir sorption isotherm data,
 614 sorption maxima (Xm), maximum buffer capacity (MBC), binding energy (b) in non-calcareous soils (n = 41) and calcareous soils (n = 33).
 615 Olsen-P values were measured on a subset of non-calcareous (n = 47) and calcareous soils (n = 14).

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	Soil pH	OM /%	Al	Fe	Ca	Langmuir Terms			Phosphorus Extracts			
						Xm	b	MBC	Morgan's P	M3-P	FeO-P	Olsen- P
						/l mg ⁻¹			/mg l ⁻¹			
						Non-calcareous soils						
Min	4.7	5.3	807	369	284	303	0.80	244	1.5	13.4	3.3	8.9
Max	6.3	18.3	1730	666	4713	625	8.00	3333	25.8	285	128	89.6
Median	5.2	9.5	1072	553	1451	476	2.56	1250	7.0	85.9	30.4	37.3
Mean	5.3	10.1	1108	540	1631	467	3.04	1417	8.15	98	35.6	40
						Calcareous soils						
Min	5.2	5.5	68.9	215	777	244	0.35	119	1.5	17.8	4.4	16.8
Max	7.1	16.3	794	642	8660	667	2.10	1000	32.9	168	69.6	57.6
Median	6.2	9.3	658	425	3539	323	0.94	303	7.1	56.1	31	27
Mean	6.2	9.9	597	432	3457	343	1.01	346	9.0	64.7	34.3	31

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619 **Captions for figures**

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621 **Figure 1.** The relationship between log transformed Langmuir maximum buffer capacity
622 (MBC) and soil pH ($R^2 = 0.55$) for the sub-set of samples for which sorption isotherms were
623 derived (n= 74).

624

625 **Figure 2.** Broken-line regression fitted to the relationship between log transformed Langmuir
626 maximum buffer capacity and extractable for the subset of samples for which sorption
627 isotherms were derived (n = 74), with a change-point derived for Al at 615 mg kg^{-1} within a
628 lower and upper confidence interval of 508 and 716 mg kg^{-1} , respectively.

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630 **Figure 3.** Ratios of Mehlich3-Al to M3-P (Al:P) plotted against (a) FeO-P and (b) Morgan's
631 P in non-calcareous (n = 76) separated out from the full data-set. A broken-line regression
632 fitted to both data-set calculated change-points for FeO-P at 43.2 mg kg^{-1} within lower and
633 upper confidence interval of 32.3 and 53.9 mg kg^{-1} , respectively. The dotted line represents
634 change-point values of Morgan's P and Al:P on the x and y axes, respectively. Morgan's P
635 change-point was derived at 7.3 mg l^{-1} within lower and upper confidence interval of 5.9 and
636 8.7 mg l^{-1} , respectively.

637

638 **Figure 4.** The Relationship between Morgan's P and (a) M3-P for both non-calcareous (n =
639 76) and calcareous soils (n = 44); and (b) Olsen-P for non-calcareous (n = 47) and calcareous
640 (n = 14) soils, with regression lines and confidence intervals showing diverging relationships
641 in both soil groups with smaller M3-P and Olsen-P values, large Morgan's P values in
642 calcareous soils.

643

644 **Figure 5.** The relationship between Morgan's P and FeO-P in non-calcareous (n = 76) and
645 calcareous (n = 44) soils with overlapping confidence intervals showing comparable values
646 of FeO-P at similar Morgan's P between both soil groups.

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