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

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25. Apr. 2024

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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21 **Summary**

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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.

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96   **Materials and methods**

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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 KH_2PO_4

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         $C/X = 1/Xm \times b + C/Xm,$ (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/Xm x b and slope 1/Xm. The linear form of the

126   Langmuir equation was then used to derive Xm, 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 (Xm, mg

129   kg^{-1}), binding energy (b, l mg^{-1}). Maximum buffer capacity (MBC, l kg^{-1}) was calculated as

130   the product of Xm 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   CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.13M HNO_3 + 0.001M 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 NaHCO$_3$, 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 Xm, 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 Xm, (r = -0.46), b (r = -0.62) and MBC (r = -0.65) whilst

182 extractable Al positively correlated with Xm, 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 Xm 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 Xm 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 Xm, 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 Xm, 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 (5.1–8 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 to 8.7 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 or 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-calacareous 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.

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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.

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

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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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561 **Table 2**. Range (min-max) of soil properties measured across samples collected from soil association listed in Table 1. Soil pH, %Organic
562 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 =
563 120). Across soil associations Langmuir sorption isotherm values were derived for a subset of samples (n = 74). Olsen extractable P (Olsen-P)
564 derived for a sub-set of soils (n = 60) did not include soil associations 30 and 14.

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							Langmuir Terms				Phosphorus Extracts	
Soil Association	pH	OM	Al	Fe	Ca	Xm	b	MBC	Morgan's P	M3-P	FeO-P	Olsen-P
		/ %			/ mg kg^{-1}		/ l mg^{-1}	/ l kg^{-1}	/ mg l^{-1}		/ mg kg^{-1}	
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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578 **Table 3**. Pearson product moment correlation matrix of r-values significant at $P = 0.05$ derived between soil pH, % organic matter (OM),
579 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
580 properties include Langmuir sorption maximum (Xm / mg kg^{-1}); binding energy, (b / l mg^{-1}) and maximum buffer capacity, (MBC / l kg^{-1}). NS
581 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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594   **Table 4**   Regression equations for relationships between logMBC and soil pH across all soils, and relationships between Morgan's P and

595   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.

596

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

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		Estimate	Standard error	t value	P	95% confidence limit	
						Lower	Upper
Figure 2	Intercept 1	6.1799	0.3299	18.73	<0.0001	5.5217	6.8381
(n = 73)	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)	Intercept 1	3.9422	0.1433	27.51	<0.0001	3.6568	4.2276
(n = 76)	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)	Intercept 1	4.2247	0.1627	25.92	<0.0001	3.9006	4.5487
(n = 76)	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).

616

| | Soil pH | OM | Al | Fe | Ca | Langmuir Terms | | | Phosphorus Extracts | | | |
| | | | | | | Xm | b | MBC | Morgan's P | M3-P | FeO-P | Olsen-P |
		/%		/mg kg^{-1}			/l mg^{-1}	/l kg^{-1}	/mg l^{-1}		/mg kg^{-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**

620

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.

629

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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