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18 **Chemical amendment of pig slurry: control of runoff related risks due to**  
19 **episodic rainfall events up to 48 h after application**

20

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31

32 **Abstract**

33

34 Losses of phosphorus (P) from soil and slurry during episodic rainfall events can contribute  
35 to eutrophication of surface water. However, chemical amendments have the potential to  
36 decrease P and suspended solids (SS) losses from land application of slurry. Current  
37 legislation attempts to avoid losses to a water body by prohibiting slurry spreading when  
38 heavy rainfall is forecast within 48 h. Therefore, in some climatic regions, slurry spreading  
39 opportunities may be limited. The current study examined the impact of three time intervals  
40 (TIs; 12, 24 and 48 h) between pig slurry application and simulated rainfall with an intensity  
41 of  $11.0 \pm 0.59 \text{ mm h}^{-1}$ . Intact grassed soil samples, 1 m long, 0.225 m wide and 0.05 m deep,  
42 were placed in runoff boxes and pig slurry or amended pig slurry was applied to the soil

43 surface. The amendments examined were: (1) commercial-grade liquid alum (8%  $\text{Al}_2\text{O}_3$ )  
44 applied at a rate of 0.88:1 [Al/total phosphorus (TP)] (2) commercial-grade liquid ferric  
45 chloride (38%  $\text{FeCl}_3$ ) applied at a rate of 0.89:1 [Fe/TP] and (3) commercial-grade liquid  
46 poly-aluminium chloride (10 %  $\text{Al}_2\text{O}_3$ ) applied at a rate of 0.72:1 [Al/TP]. Results showed  
47 that an increased TI between slurry application and rainfall led to decreased P and SS losses  
48 in runoff, confirming that the prohibition of land-spreading slurry if heavy rain is forecast in  
49 the next 48 h is justified. Averaged over the three TIs, the addition of amendment reduced all  
50 types of P losses to concentrations significantly different ( $p<0.05$ ) to those from unamended  
51 slurry, with no significant difference between treatments. Losses from amended slurry with a  
52 TI of 12 h were less than from unamended slurry with a TI of 48 h, indicating that chemical  
53 amendment of slurry may be more effective at ameliorating P loss in runoff than current TI-  
54 based legislation. Due to the high cost of amendments, their incorporation into existing  
55 management practices can only be justified on a targeted basis where inherent soil  
56 characteristics deem their usage suitable to receive amended slurry.

57

58 **Keywords:** pig slurry, runoff, P sorbing amendments, Nitrates Directive, Water Framework  
59 Directive, phosphorus, suspended solids

60

## 61 **Introduction**

62

63 During episodic rainfall events, phosphorus (P) and reactive nitrogen ( $\text{N}_r$ ) fluxes from critical  
64 (soil) and incidental (e.g. slurry or fertiliser application) sources can contribute to  
65 anthropogenic eutrophication of surface water (Preedy et al. 2001; Kleinmann et al. 2006;  
66 Wall et al. 2011). European Union (EU) legislation attempts to optimise nutrient use on  
67 agricultural land and to avoid losses to water bodies. The Nitrates Directive (OJEC 1991;

68 Montenev 2001) has been ratified into national legislation in Ireland and limits the  
69 magnitude, timing and placement of inorganic and organic fertilizer applications (Jordan et  
70 al. 2012). Specifically, it stipulates a mandatory closed period for slurry spreading during  
71 winter. Slurry application is limited on soils with a high soil test P (e.g. Morgan's  $P > 8 \text{ mg}$   
72  $\text{L}^{-1}$ ), thereby restricting the available land for application (Nolan et al. 2012). Additionally,  
73 slurry spreading is prohibited when heavy rainfall is forecast within 48 h of application.  
74 Therefore, slurry spreading opportunities may be limited, especially in wet years or in areas  
75 where soil trafficability is limited due to wet or saturated soil conditions.

76

77 Even though there is very clear evidence that P losses in runoff are reduced with increasing  
78 time interval (TI) between slurry application and the occurrence of a rainfall-runoff event  
79 (Daverede et al. 2004; Hart et al. 2004), most studies have investigated the effect of  
80 cumulative rainfall events. Only a few studies have looked at the effect of the TI between  
81 slurry application and the first rainfall event (Sharpley 1997; Smith et al. 2007; Allen and  
82 Mallarino 2008). Moreover, none of these studies assessed a range of TIs shorter than 48 h,  
83 which is the limit set by Irish and UK regulations. Assessing the risk of runoff at TIs within  
84 these 48 h is highly relevant, as the occurrence of heavy rain can often not be ruled out in the  
85 highly unpredictable North Atlantic climate (McDonald et al. 2007; Creamer et al. 2010). In  
86 addition, this would provide evidence that a 48 h limit does not unnecessarily restrict the  
87 opportunity of farmers to apply slurry. To our best knowledge, there are no studies that  
88 address the validity of adhering to a 48-h dry period between application and the first heavy  
89 rainfall event, apart from work by Serrenho et al. (2012), who found that adherence to a  
90 minimum TI of 48 h between application of dairy soiled water and rainfall was prudent to  
91 reduce incidental P losses in runoff. Investigating the development of P losses during first

92 rainfall events within 48 h after application can shed more light on the validity and  
93 effectiveness of this measure.

94  
95 Measures to effectively control agricultural P transfer from soil to water include chemical  
96 amendment of slurry. Alum, aluminium chloride ( $\text{AlCl}_3$ ), lime and ferric chloride ( $\text{FeCl}_3$ )  
97 have been shown to significantly reduce P losses in surface runoff arising from the land  
98 application of dairy cattle slurry (Brennan et al. 2011, 2012), dairy soiled water (Serrenho et  
99 al. 2012), poultry litter (Moore et al. 1999, 2000) and pig slurry (Dao 1999; Dou et al. 2003;  
100 Smith et al. 2001, 2004; O' Flynn et al. 2012a, b). In particular, O' Flynn et al. (2012b)  
101 showed that the runoff losses from amended pig slurry 48 h after application could be  
102 reduced to levels similar to the soil-only treatment. This warrants the effort of assessing the  
103 effectiveness of these additives at TIs of less than 48 h between application and first rainfall  
104 event.

105  
106 Therefore, the aim of this study was to investigate the effect of TI (12, 24 and 48 h) between  
107 pig slurry application and first rainfall event on the losses of P and suspended solids (SS) in  
108 runoff, and to assess the efficacy of adding chemical amendments in reducing losses at these  
109 three TIs.

110  
111 **Materials and Methods**

112  
113 **Slurry collection and characterisation**

114  
115 Pig slurry was taken from an integrated pig unit in Teagasc Research Centre, Moorepark,  
116 Fermoy, Co. Cork, Ireland in April 2012. The sampling point was a valve on an outflow pipe

117 between two holding tanks, which were sequentially placed after a holding tank under slats  
118 on which no bedding materials were used. To ensure a representative sample, this valve was  
119 turned on and left to run for a few minutes before taking a sample. The slurry was stored  
120 inside a cold-room fridge at 10°C prior to testing. Total P (TP) and total nitrogen (TN) were  
121 determined using persulfate digestion. Ammonium-N ( $\text{NH}_4^+\text{-N}$ ) was determined by adding 50  
122 ml of slurry to 1 L of 0.1M HCl, shaking for 30 min at 200 rpm, filtering through no. 2  
123 Whatman filter paper, and analysing using a nutrient analyser (Konelab 20, Thermo Clinical  
124 Labsystems, Finland). Slurry pH was determined using a pH probe (WTW, Germany). Dry  
125 matter content was determined by drying at 105°C for 24 h. The physical and chemical  
126 characteristics of the pig slurry used in this experiment and characteristic values of pig slurry  
127 from other farms in Ireland are presented in Table 1.

128

### 129 **Pig slurry amendment**

130

131 Amendments for the present study were chosen based on effectiveness of P sequestration and  
132 feasibility criteria (cost and potential for metals release to the environment; Table 2)) as  
133 determined by O' Flynn et al. (2012a, b). The amendment rates, which were applied on a  
134 stoichiometric basis were: (1) commercial grade liquid alum (8%  $\text{Al}_2\text{O}_3$ ) applied at a rate of  
135 0.88:1 [Al/TP] (2) commercial-grade liquid ferric chloride (38%  $\text{FeCl}_3$ ) applied at a rate of  
136 0.89:1 [Fe/TP]; and (3) commercial-grade liquid poly-aluminium chloride (PAC) (10 %  
137  $\text{Al}_2\text{O}_3$ ) applied at a rate of 0.72:1 [Al/TP]. The compositions of the amendments used are the  
138 same as those used in O' Flynn et al. (2012a, b).

139

### 140 **Soil collection and analysis**

141

142 Intact grassed soil samples 1.2 m long, 0.3 m wide, 0.1 m deep (n=45) were collected from  
143 permanent grassland, which had not received fertiliser applications for more than 10 yr, in  
144 Galway City, Ireland (53°16'N, -9°02'E). Samples were cut out of the ground with a spade  
145 and, to avoid cracking, placed carefully on 1.5 m long, 0.5 m wide timber boards. Between  
146 collection and use, soil samples were stored externally to prevent drying. Soil samples (n=3),  
147 taken from the upper 0.1 m from the same location, were oven dried at 40 °C for 72 h,  
148 crushed to pass a 2 mm sieve and analysed for Morgan's P (the national test used for the  
149 determination of plant available P in Ireland) using Morgan's extracting solution (Morgan  
150 1941). Soil pH (n=3) was determined using a pH probe and a 2:1 ratio of deionised water to  
151 soil. The particle size distribution was determined using a sieving and pipette method (British  
152 Standards Institution 1990a) and the organic content of the soil was determined using the loss  
153 on ignition test (British Standards Institution 1990b). The soil used was a well-drained, sandy  
154 loam textured, acid brown earth (WRB classification: Cambisol) (58% sand, 29% silt, 14%  
155 clay) with a soil test P of  $2.8 \pm 0.5 \text{ mg L}^{-1}$ , making it a P index 1 soil according to The  
156 European Communities (Good Agricultural Practice for Protection of Waters) Regulations  
157 2010 (hereafter referred to as S.I. No. 610 of 2010); total potassium of  $203 \text{ mg L}^{-1}$ , a pH of  
158  $6.4 \pm 0.3$  and an organic matter content of  $5 \pm 2\%$ .

159

### 160 **Rainfall simulation study**

161

162 The following treatments were examined within 21 days of sample collection: (1) a grassed  
163 sod-only treatment with no slurry applied, (2) a grassed sod with unamended slurry (the  
164 slurry control) applied at a rate of  $19 \text{ kg TP ha}^{-1}$  and (3) grassed sods receiving amended  
165 slurry applied at a rate of  $19 \text{ kg TP ha}^{-1}$ . Three replications of each treatment were subject to  
166 rainfall at a TI between application and rainfall of either 12 (TI 1), 24 (TI 2) or 48 h (TI 3).

167

168 Stainless steel laboratory runoff boxes, constructed by a steel fabricator, 1 m long, 0.225 m  
169 wide and 0.075 m deep, with side walls of 0.025 m higher than the grassed sods, were used in  
170 this experiment. The runoff boxes were positioned under a rainfall simulator. The rainfall  
171 simulator consisted of a single 1/4HH-SS14SQW nozzle (Spraying Systems Co., Wheaton,  
172 IL, USA) attached to a 4.5 m high metal frame, and calibrated to achieve an intensity of  
173  $11.0 \pm 0.59 \text{ mm h}^{-1}$  and a droplet impact energy of  $260 \text{ kJ mm}^{-1} \text{ ha}^{-1}$  at 85% uniformity after  
174 Regan et al. (2010). The source for the water used in the rainfall simulations had a dissolved  
175 reactive P (DRP) concentration of less than  $0.005 \text{ mg L}^{-1}$ , a pH of  $7.7 \pm 0.2$  and an electrical  
176 conductivity of  $0.44 \text{ dS m}^{-1}$ . Each runoff box had 5 mm diameter drainage holes, spaced at  
177 distances of 0.3 m centre to centre, positioned in a line and spanning the length of the base,  
178 after Regan et al. (2010). Muslin cloth was placed at the base of each runoff box before  
179 packing the sods to prevent soil loss. Immediately prior to the start of each experiment, the  
180 sods were trimmed and packed in the runoff boxes. To prevent cracking, sods were first  
181 trimmed into two 0.5 m lengths and then placed in the runoff box. Each sod was then butted  
182 against its adjacent sod to form a continuous surface. Molten candle wax was used to seal any  
183 gaps between the soil and the sides of the runoff box, while the joints between adjacent soil  
184 samples did not require molten wax. The packed sods were then saturated using a rotating  
185 disc, variable-intensity rainfall simulator (after Williams et al. 1997), and left to drain for 24  
186 h by opening the 5 mm diameter drainage holes before continuing with the experiment. At  
187 this point, when the soil was at approximately field capacity, slurry and amended slurry were  
188 spread on the packed sods and the drainage holes were sealed. They remained sealed for the  
189 duration of the experiment. At  $t = 12, 24$  or  $48 \text{ h}$ , the sods were subjected to a rainfall event,  
190 and each event lasted for a duration of 30 min after runoff began. Different sods were used  
191 for each rainfall event. Surface runoff samples were collected in 5 min intervals over the 30



192 min period and in the time period subsequent to the when the rainfall simulator was turned  
193 off, until no further runoff samples were available.

194

195 Runoff water samples were tested for pH. A subsample was passed through a 0.45 µm filter  
196 and analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo  
197 Clinical Labsystems, Finland). Filtered (passed through a 0.45 µm filter) and unfiltered  
198 subsamples, collected at 10, 20 and 30 min after runoff began and any subsequent runoff  
199 once rainfall ceased, underwent acid persulfate digestion and were analysed colorimetrically  
200 for total dissolved P (TDP) and TP using a nutrient analyser (Konelab 20, Thermo Clinical  
201 Labsystems, Finland. Particulate phosphorus (PP) was calculated by subtracting TDP from  
202 TP. Dissolved unreactive P was calculated by subtracting DRP from TDP. Suspended solids  
203 were tested by vacuum filtration of a well-mixed (previously unfiltered) subsample through  
204 Whatman GF/C (pore size, 1.2 µm) filter paper. Prior to filtration, the filter paper was  
205 weighed. After filtration, the filter paper was dried at 105°C for 24 h and reweighed.

206

## 207 **Statistical analysis**

208

209 The data was analysed in R (version 2.15.1, 32 bit) and IBM SPSS 20 using analysis of  
210 variance implemented via a general linear model. There were five levels of treatment (soil-  
211 only, slurry-only (the study control), and slurry treated with alum, PAC and FeCl<sub>3</sub>) and three  
212 levels of the time factor (12, 24 and 48 h). Diagnostic plots indicated that a logarithmic  
213 transformation of the response variable was desirable when analysing the effects of the  
214 predictor variables on the flow weighted mean concentrations (FWMCs, calculated by  
215 dividing the total load over a rainfall event by the total flow) of DRP, dissolved unreactive P,  
216 TDP, PP and TP, if the normal distributional assumptions of the analysis were to be met. No

217 transformation was performed for the analysis of SS. Probability values of  $p > 0.05$  were  
218 deemed not to be significant.

219

## 220 **Results**

221

### 222 **Phosphorus in runoff**

223

224 The FWMC of P in runoff from the soil-only treatment showed no statistically significant  
225 differences between TIs, with average TP and TDP FWMCs of 0.35 and 0.21 mg L<sup>-1</sup>  
226 (corresponding to loads of 2.48 and 1.49 mg m<sup>-2</sup>), respectively (Fig. 1, Table 2). At all TIs, P  
227 losses of all forms increased significantly ( $p < 0.05$ ) with slurry application compared with the  
228 soil only treatment (Fig. 1). The increase in losses was particularly high for PP, and averaged  
229 over the three TIs, the PP in runoff from the soil-only contributed 40% of the TP (Table 2)  
230 compared to 67% of the runoff from slurry-only. For the slurry-only treatment, losses of P in  
231 runoff significantly ( $p < 0.05$ ) decreased with increasing TI between application and rainfall.  
232 The FWMC of TP and TDP decreased from 8.2 and 3.4 mg L<sup>-1</sup> (corresponding to loads of  
233 45.7 and 18.9 mg m<sup>-2</sup>), respectively, at TI 1 to 3.6 and 1.1 mg L<sup>-1</sup> (23.5 and 7.5 mg m<sup>-2</sup>) at TI  
234 3 (Fig. 1).

235

236 In general, the addition of chemical amendment significantly ( $p < 0.05$ ) reduced concentrations  
237 of all forms of P lost in runoff at each TI to below the lowest losses from slurry-only, i.e. at a  
238 TI of 48 h (Fig. 1). However, with the exception of DRP, all forms of P losses in runoff from  
239 amended slurry were significantly ( $p < 0.05$ ) different to those from soil-only (Table 2). There  
240 were generally no significant differences between amendments for P losses in runoff. Time

241 interval had no significant effect on P losses from amended slurry. There was no evidence of  
242 any significant interaction between time and treatment type.

243

### 244 **Suspended solids and pH in runoff**

245

246 Loses of SS in runoff from soil-only did not change significantly with TI, with FWMCs of  
247 15.5, 16.9 and 15.6 mg L<sup>-1</sup> (corresponding to loads of 134, 116 and 118 mg m<sup>-2</sup>) after TIs 1, 2  
248 and 3, respectively (Fig. 2). Application of slurry increased SS losses significantly ( $p<0.001$ )  
249 to levels over 30 times that of soil-only at TI 1 (482 mg L<sup>-1</sup> or 2780 mg m<sup>-2</sup>). Similar to the  
250 trends observed in P losses for the slurry-only treatment, losses of SS in runoff decreased  
251 with increasing TI between slurry application and rainfall, with statistically significant  
252 differences ( $p<0.05$ ) between each TI. Similar to the P observations, losses of SS in runoff  
253 from amended slurry at all TIs were less than the lowest losses from unamended slurry at TI  
254 3 ( $p<0.05$ ). Whilst diagnostic plots were not entirely satisfactory for SS, all results were  
255 extremely clear-cut and there can be no doubt concerning the significance, or otherwise, of  
256 the results reported. The variable pH proved to be insignificant in all cases.

257

### 258 **Discussion**

259

#### 260 **Phosphorus in runoff from soil-only**

261

262 The soil used in the present study was P deficient (P index 1), which would not normally be  
263 expected to pose a danger of P losses to the environment (Schulte et al. 2010) as such a soil  
264 requires additional nutrients to build up soil P reserves. Phosphorus concentrations in runoff  
265 from the soil only treatment were often above the Irish surface water regulation of 0.035 mg

266 reactive P L<sup>-1</sup> (S.I. No. 272 of 2009), but overall loads were small and therefore any  
267 deleterious effects to a greater scale cannot be inferred. In the field, rainfall would typically  
268 be less intense, and the soil would have the capacity for vertical drainage. As a result, the  
269 experiment replicated a worst-case scenario in terms of potential P loss from this soil.  
270 Therefore, while P losses from the runoff boxes may be used to compare the effects of  
271 chemical amendments and TI, they are not an accurate measure of P loss concentration or  
272 load to a surface water body that might be expected at field scale.

273

#### 274 **Phosphorus in runoff from unamended slurry**

275

276 Decreased losses of P in runoff with increasing TI between application and rainfall have also  
277 been found in previous research—but at TIs significantly greater than those examined in the  
278 present study. In a plot study, Smith et al. (2007) spread pig slurry at 35 kg P ha<sup>-1</sup> and found  
279 that at 30 min rainfall events, each with an intensity of 100 mm h<sup>-1</sup>, DRP concentrations in  
280 runoff reduced from 8.4 mg DRP L<sup>-1</sup> at a TI of 1 day to 2.6 mg DRP L<sup>-1</sup> at a TI of 29 days.  
281 Allen and Mallarino (2008) spread pig slurry in a plot study at varying rates up to 108 kg P  
282 ha<sup>-1</sup> and found that during 30-min rainfall events, each with an intensity of 76 mm h<sup>-1</sup>, DRP  
283 and TP loads in runoff were 3.8 and 1.6 times lower at a TI of 10-16 days than at a TI of less  
284 than 24 h. The trend of an initial peak followed by a gradual reduction may be due to the  
285 interaction of the applied P and the conversion from soluble to increasingly recalcitrant forms  
286 over time (Edwards and Daniel 1993). The current study indicates that this process already  
287 starts within 24 h after application, and confirms that the prohibition of the land-spreading of  
288 slurry, if heavy rain is forecast in the next 48 h (S.I. No. 610 of 2010), is justified.

289

290 The extra PP lost in runoff from unamended slurry, associated with sediment and organic  
291 material in agricultural runoff, may provide a variable, but long-term, source of P in lakes  
292 (Sharpley et al. 1992), and as it is generally bound to the minerals (particularly iron (Fe), Al,  
293 and calcium (Ca)) and organic compounds contained in soil, it constitutes a long-term P  
294 reserve of low bioavailability (Regan et al. 2010).

295

### 296 **The effect of slurry amendment on P losses**

297

298 The addition of amendment resulted in reduced P losses in runoff compared to unamended  
299 slurry, with losses reduced at each TI to below the lowest losses from slurry only. There  
300 appeared to be little difference in runoff losses of P between the different amendments (Table  
301 2). Higher losses in runoff from amended slurry than soil-only is because chemical  
302 amendment of slurry will only reduce the incidental P losses to the environment, but will not  
303 reduce chronic (long-term) P losses from the soil. In a field-based study, Smith et al. (2004)  
304 found that  $\text{AlCl}_3$ , added at 0.75% of final slurry volume to slurry from pigs on a phytase-  
305 amended diet, could reduce runoff DRP by 73%. In another field-based study, Smith et al.  
306 (2001) found that alum and  $\text{AlCl}_3$ , added at a stoichiometric ratio of 0.5:1 Al/TP to pig slurry,  
307 achieved reductions of 33 and 45%, respectively, in runoff water, and reductions of 84% in  
308 runoff water when adding both alum and  $\text{AlCl}_3$  at 1:1 Al/TP.

309

310 Investigation of chemical amendment effectiveness on two soils using identical amendments,  
311 spreading rate and TI (Table 3) produced varied results due to differing soil characteristics.  
312 Both soils were of a similar texture but have different levels of soil organic carbon. Even  
313 though the current study was conducted on a P index 1 soil and had a lower chronic TP loss  
314 than measured by O' Flynn et al. (2012b), incidental losses from slurry were higher, but not

315 significantly so. Additionally, the effectiveness of the amendments (PAC, in particular) was  
316 much lower than reported by O' Flynn et al. (2012b; Table 3). This may be explained by  
317 differences in soil characteristics between the two experiments: the soil used by O' Flynn et  
318 al. (2012b) had a higher buffering capacity (i.e. more binding sites to retain added P) than  
319 that of the current study, due to differences in soil composition, including pH and organic  
320 matter. This reduction in effectiveness may also be the cause for little difference in P losses  
321 between the different amendments (Table 2). The effectiveness of slurry amendments is  
322 hence soil specific and should therefore be examined in future studies.

323

324 Based on the results from this study, runoff from amended slurry will have reduced P losses  
325 regardless of TI between landspreading and the occurrence of rainfall, indicating that  
326 chemical amendment may be more effective in reducing P losses than the current TI-based  
327 legislation.

328

### 329 **Suspended solids and pH in runoff**

330

331 As is the case with P, the reduction of SS was also related to the flocculating properties of the  
332 amendments. As well as removing PP from suspension, they also aid in adhesion of slurry  
333 particles, making them less prone to loss in runoff (Brennan et al. 2011). Apart from soil-  
334 only, losses of SS in runoff were all well above  $35 \text{ mg L}^{-1}$ , the treatment standard necessary  
335 for discharge to receiving waters (S.I. No 419 of 1994). However, whilst the results from this  
336 laboratory study may be used to compare the effects of chemical amendments and TI, they  
337 are not intended as a measure of actual losses to surface water bodies at field-scale.

338

339 The effect of amendments on slurry pH is a potential barrier to their implementation as it  
340 affects P sorbing ability (Penn et al. 2011) and ammonia (NH<sub>3</sub>) emissions from slurry  
341 (Lefcourt and Messinger 2001). However, the results from this laboratory experiment, similar  
342 to previous studies (Smith et al. 2004; O' Flynn et al. 2012b), showed that there was no effect  
343 on the pH of the runoff water due to the use of amendments. However, further investigation  
344 would need to be undertaken to confirm that pollution swapping (the increase in one pollutant  
345 as a result of a measure introduced to reduce another pollutant (Healy et al. 2012)) does not  
346 occur.

347

#### 348 **Targeted use of amendments**

349

350 Due to high costs involved (O' Flynn et al. 2012a), use of chemical amendments in slurry for  
351 land application can only be justified on a targeted basis, in particular: (1) soils with high  
352 mobilisation potential, soil test P and hydrological transfer potential to surface water, i.e. a  
353 critical source area and (2) at times when storage capacity becomes the critical factor, i.e.  
354 towards the end of the open period when unpredictable weather conditions would normally  
355 prohibit slurry spreading. In these cases, the adoption of the use of chemical amendment of  
356 slurry as part of a programme of measures would be justified. However, chemical  
357 amendments should only be used on soils that have been extensively tested for suitability.

358 The difference in removals experienced in the current study and by O' Flynn et al. (2012b;  
359 Table 3) demonstrates the impact that soil type has on the efficacy of chemical amendment of  
360 pig slurry. The future uptake of such a mitigation strategy is dependent on the additional cost  
361 being considered a worthwhile expense, based on weather conditions and regulatory  
362 constraints at the time. If climatic conditions and legislation results in inadequate periods

363 during which to spread slurry, and exerts pressure on slurry storage facilities, then chemical  
364 amendment may be seen as the most cost-effective and feasible option.

365

## 366 **Conclusions**

367

368 The excessively high losses of P in runoff at TIs of less than 48 h after slurry application,  
369 combined with the strong decrease of P losses within this time frame, confirm that the  
370 prohibition of land-spreading slurry if heavy rain is forecast in the next 48 h (S.I. No. 610 of  
371 2010) is justified. Chemical amendment of pig slurry was effective at decreasing P and SS  
372 losses from the slurry. Runoff P losses from amended slurry were lower than from  
373 unamended slurry regardless of TI between land application and the occurrence of rainfall,  
374 indicating that chemical amendment may be more effective at reducing P losses than current  
375 TI-based legislation. The cumulative deposition of slurry over time, coupled with  
376 unpredictable weather patterns, increases the need for amendment, as leaching and overland  
377 flow are all possible vectors for pollution. The tightening of environmental legislation or the  
378 rigorous enforcement of current Water Framework Directive (European Commission 2000)  
379 legislation means that investment in P reduction will become justified. Due to the high cost of  
380 amendments, their incorporation into existing management practices can only be justified on  
381 a targeted basis, in particular: (1) critical source areas and (2) towards the end of the open  
382 period when unpredictable weather conditions would normally prohibit slurry spreading.  
383 However, chemical amendments should only be used on soils that are suitable. There is a  
384 pervading difficulty in gaining acceptance for new technologies by farmers, and so strategies  
385 such as those suggested by this study may never be implemented at farm scale. Future work  
386 must be carried out on the refinement of spreading lands within critical source areas based on  
387 soil suitability to receive amended slurry.



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Chemical amendment has also been used for the poultry and dairy industries, but may also have the potential to be used in the treatment of wastes from other agricultural industries and sludge from wastewater treatment. If chemical amendment becomes a more prevalent practice, then the cost of employing it as a mitigation measure may decrease, making it an even more attractive option. Although encouraging, the effectiveness of the amendments examined in this study must be validated at field scale.

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560 **Figure Captions**

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562 **Fig. 1** Histogram of flow-weighted mean concentrations ( $\text{mg L}^{-1}$ ) for dissolved reactive  
563 phosphorus (DRP), dissolved un-reactive phosphorus (DUP) and particulate phosphorus (PP)  
564 in runoff at time intervals of 12, 24 and 48 h after land application of pig slurry

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566 **Fig. 2** Histogram of average flow-weighted mean concentration of suspended solids (SS) ( $\text{mg}$   
567  $\text{L}^{-1}$ ) in runoff at time intervals of 12, 24 and 48 h after land application of pig slurry

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585 Table 1 Physical and chemical characteristics<sup>a</sup> of the pig slurry used in this experiment and  
 586 characteristic values of pig slurry from other farms in Ireland

TP	TN	TK	NH <sub>4</sub> <sup>+</sup> -N	pH	DM	Reference
(mg L <sup>-1</sup> )			(%)			
482±37	3,850±20		2250 ±72	7.37 ± 0.07	3.22± 0.15	The present study
800	4,200					S.I. No. 610 of 2010
1630	6,621	2,666			5.77	McCutcheon 1997 <sup>b</sup>
900±7	4,600±21	2,600±10			3.2±2.3	O' Bric 1991 <sup>b</sup>

<sup>a</sup>TP total P; TN total N; TK total K; DM dry matter. <sup>b</sup>Values changed to mg L<sup>-1</sup> assuming densities of 1 kg L<sup>-1</sup>.

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609 Table 2 Flow-weighted mean concentrations (mg L<sup>-1</sup>) averaged over three time intervals, application costs per tonne, metal application rate (kg  
 610 ha<sup>-1</sup>), and removals (%) for dissolved reactive P (DRP), dissolved un-reactive P (DUP), total dissolved P (TDP), particulate P (PP), total P (TP)  
 611 and suspended solids (SS)

	DRP	Removal	DUP	Removal	TDP	Removal	PP	Removal	TP	Removal	SS	Removal	Costs	Metals
	mg L <sup>-1</sup>	%	mg L <sup>-1</sup>	%	mg L <sup>-1</sup>	%	mg L <sup>-1</sup>	%	mg L <sup>-1</sup>	%	mg L <sup>-1</sup>	%	€ tonne <sup>-1</sup>	kg ha <sup>-1</sup>
Soil Only	0.10 <sup>a</sup>	-	0.11 <sup>a</sup>	-	0.21 <sup>a</sup>	-	0.14 <sup>a</sup>	-	0.35 <sup>a</sup>	-	15.98 <sup>a</sup>	-	-	-
Slurry Only	1.34 <sup>b</sup>	-	0.60 <sup>c</sup>	-	1.94 <sup>c</sup>	-	3.85 <sup>c</sup>	-	5.78 <sup>c</sup>	-	377.60 <sup>c</sup>	-	-	-
Alum	0.21 <sup>a</sup>	84	0.28 <sup>b</sup>	53	0.49 <sup>b</sup>	74	1.78 <sup>b</sup>	54	2.27 <sup>b</sup>	61	101.30 <sup>b</sup>	73	150	16.72 <sup>e</sup>
FeCl <sub>3</sub>	0.21 <sup>a</sup>	84	0.19 <sup>b</sup>	69	0.40 <sup>b</sup>	80	1.48 <sup>b</sup>	61	1.88 <sup>b</sup>	67	139.94 <sup>b</sup>	63	250	16.91 <sup>f</sup>
PAC	0.22 <sup>a</sup>	84	0.26 <sup>b</sup>	56	0.48 <sup>b</sup>	75	2.01 <sup>b</sup>	48	2.49 <sup>b</sup>	57	135.68 <sup>b</sup>	64	280	13.68 <sup>e</sup>

<sup>abcd</sup> Means in a column, which do not share a superscript, were significantly different ( $p < 0.05$ ). <sup>e</sup>Spreading rate of Al. <sup>f</sup>Spreading rate of Fe.

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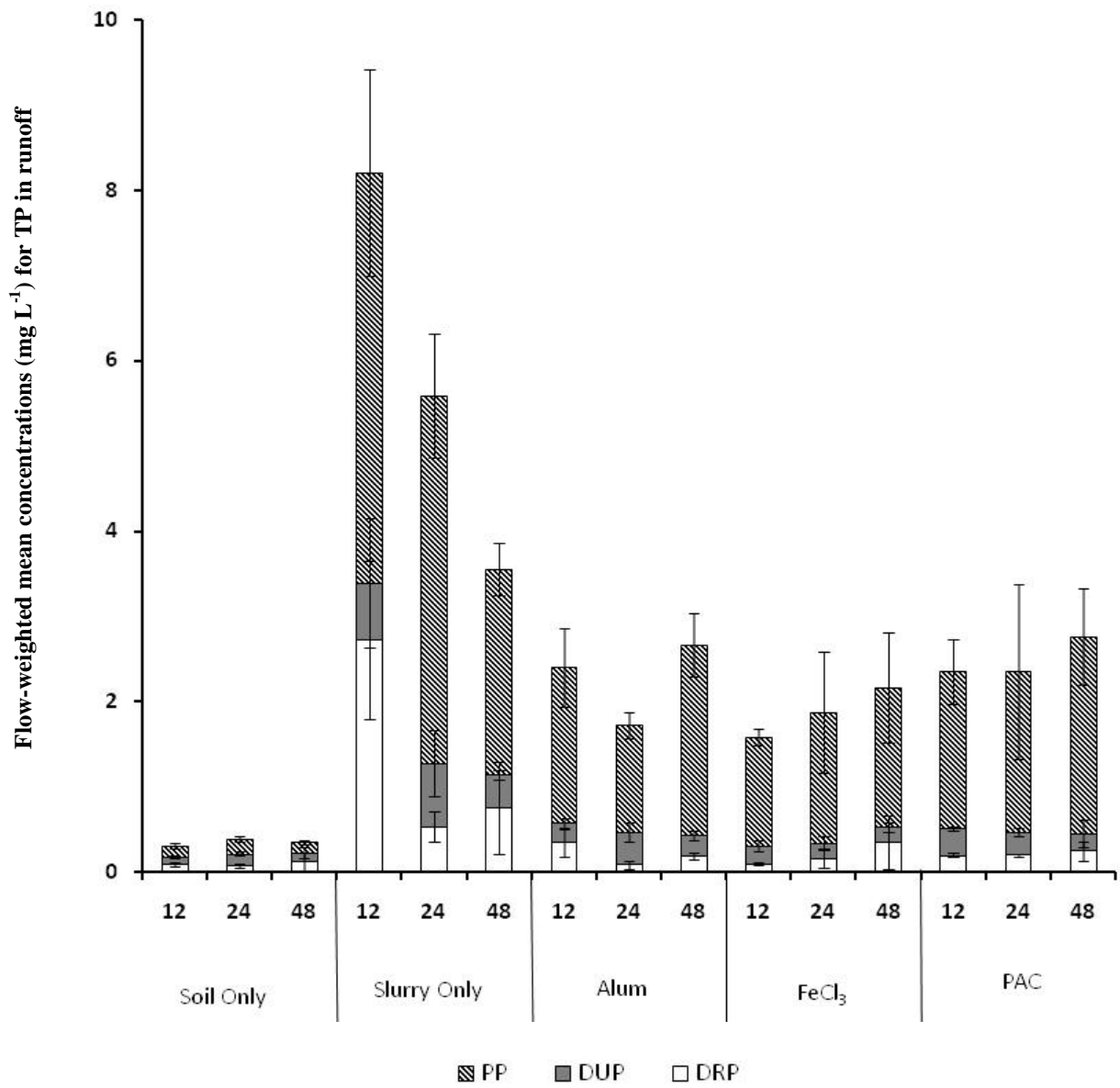
618 Table 3 Comparison of flow-weighted mean concentrations ( $\text{mg L}^{-1}$ ) of TP in runoff from  
 619 two different soils with identical amendments, spreading rates and TIs<sup>a</sup>

	Soil 1		Soil 2	
Study	Current study		O' Flynn et al. (2012b)	
Soil texture	Sandy loam		Sandy loam	
Organic matter (%)	5±2		13±0.1	
Soil organic carbon (%)	2.8		7.4	
Soil pH	6.4±0.3		7.65±0.06	
Parent material	Granite		Limestone	
P index	1		4	
Morgan's P ( $\text{mg L}^{-1}$ )	2.8±0.5		16.72±3.58	
Runoff results	TP	Removal	TP	Removal
	$\text{mg L}^{-1}$	(%)	$\text{mg L}^{-1}$	(%)
Soil-only	0.36		0.62	
Slurry-only	3.65		2.68	
PAC	2.77	24%	0.79	71%
Alum	2.08	43%	1.39	48%
FeCl <sub>3</sub>	2.17	41%	1.14	57%

<sup>a</sup>Runoff results are from rainfall events at TIs of 48 h, which occurred in both studies.

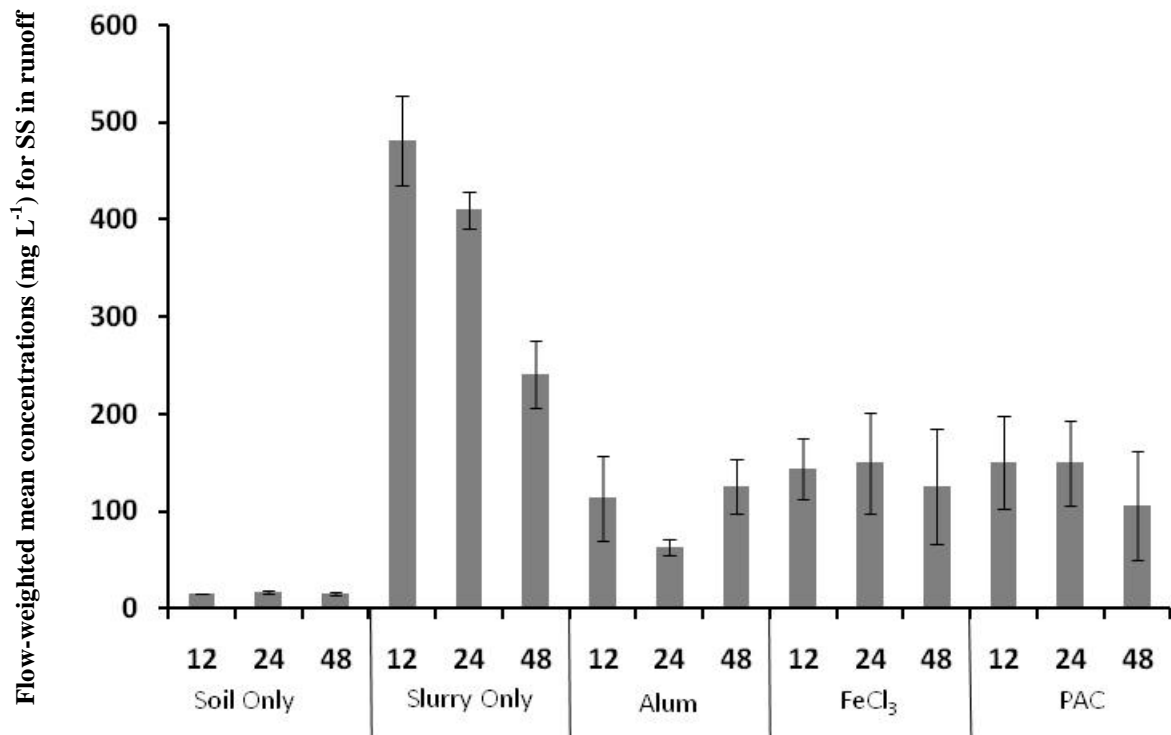
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650 Fig. 1



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666 Fig. 2



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