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4

5 **Impact of pig slurry amendments on phosphorus,** 6 **suspended sediment and metal losses in laboratory runoff** 7 **boxes under simulated rainfall**

8

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19

20 **Abstract**

21

22 Losses of phosphorus (P) when pig slurry applications to land are followed by a rainfall event

23 or losses from soils with high P contents can contribute to eutrophication of receiving waters.

24 The addition of amendments to pig slurry spread on high P Index soils may reduce P and

25 suspended sediment (SS) losses. This hypothesis was tested at laboratory-scale using runoff

26 boxes under simulated rainfall conditions. Intact grassed soil samples, 100 cm-long, 22.5 cm-
27 wide and 5 cm-deep, were placed in runoff boxes and pig slurry or amended pig slurry was
28 applied to the soil surface. The amendments examined were: (1) commercial grade liquid
29 alum (8% Al_2O_3) applied at a rate of 0.88:1 [Al: total phosphorus (TP)] (2) commercial-grade
30 liquid ferric chloride (38% FeCl_3) applied at a rate of 0.89:1 [Fe:TP] and (3) commercial-
31 grade liquid poly-aluminium chloride (PAC) (10 % Al_2O_3) applied at a rate of 0.72:1 [Al:TP].
32 The grassed soil was then subjected to three rainfall events ($10.3 \pm 0.15 \text{ mm h}^{-1}$) at time
33 intervals of 48, 72, and 96 h following slurry application. Each sod received rainfall on 3
34 occasions. Results across three rainfall events showed that for the control treatment, the
35 average flow weighted mean concentration (FWMC) of TP was 0.61 mg L^{-1} , of which 31%
36 was particulate phosphorus (PP), and the average FWMC of SS was 38.1 mg L^{-1} . For the
37 slurry treatment, there was an average FWMC of 2.2 mg TP L^{-1} , 47% of which was PP, and
38 the average FWMC of SS was 71.5 mg L^{-1} . Ranked in order of effectiveness from best to
39 worst, PAC reduced the average FWMC of TP to 0.64 mg L^{-1} (42% PP), FeCl_3 reduced TP to
40 0.91 mg L^{-1} (52% PP) and alum reduced TP to 1.08 mg L^{-1} (56% PP). The amendments were
41 in the same order when ranked for effectiveness at reducing SS: PAC (74%), FeCl_3 (66%) and
42 alum (39%). Total phosphorus levels in runoff plots receiving amended slurry remained
43 above those from soil only, indicating that, although incidental losses could be mitigated by
44 chemical amendment, chronic losses from the high P index soil in the current study could not
45 be reduced.

46

47 **Keywords:** pig slurry, amendments, runoff, phosphorus, suspended sediment, metals

48

49 1. Introduction

50

51 The European Union Water Framework Directive (WFD) (European Commission (EC),
52 2000) aims to achieve ‘at least’ good ecological status for all water bodies in all member
53 states by 2015 with the implementation of Programmes of Measures (POM) by 2012. Taking
54 Ireland as an example, The European Communities (Good Agricultural Practice for
55 Protection of Waters) Regulations 2010 (hereafter referred to as statutory instrument (S.I.)
56 No. 610 of 2010) is Ireland’s POM, which satisfies both the WFD and the Nitrates Directive
57 (European Economic Community (EEC), 1991). The Nitrates Directive promotes the use of
58 good farming practices to protect water quality across Europe by implementing measures to
59 prevent nitrates from agricultural sources polluting a water body. S .I. No. 610 of 2010
60 imposes a limit on the amount of livestock manure that can be applied to land. As part of this,
61 the maximum amount of livestock manure that may be spread on land, together with manure
62 deposited by the livestock, cannot exceed 170 kg of nitrogen (N) and 49 kg phosphorus (P)
63 $\text{ha}^{-1} \text{ year}^{-1}$. This limit is dependent on grassland stocking rate and soil test P (STP). Presently,
64 these limits may only be exceeded: (1) when spreading spent mushroom compost, poultry
65 manure, or pig slurry (2) if the size of a holding has not increased since 1st August 2006 and
66 (3) if the N application limit is not exceeded (S.I. No. 610 of 2010). The amount by which
67 these limits can be exceeded will be reduced gradually to zero by 1st January, 2017 (Table 1).
68 This will have the effect of reducing the amount of land available for the application of pig
69 slurry and may lead to the need for pig export, which itself becomes energetically
70 questionable at distances over 50 km (Feally and Schroder, 2008). These new regulations will
71 have an impact on the pig industry, in particular, as it is focused in relatively small areas of
72 Ireland.

73

74 At present, pig slurry in Ireland is almost entirely landspread (B. Lynch, pers. comm.). The
75 application of slurry in excess of crop requirements can give rise to elevated STP

76 concentrations, which may take years-to-decades to be reduced to agronomically optimum
77 levels (Schulte et al., 2010). Typically, fields neighbouring farm yards have highest soil P
78 index as they receive preferential organic fertilizer application (Wall et al., 2011). Soil P
79 Index categories of 1 (deficient) to 4 (excessive) are used to classify STP concentrations in
80 Ireland (Schulte et al., 2010). The soil P Index is based on the Morgan's extraction, with a
81 STP of $> 8\text{mg L}^{-1}$ classified as P index 4 (S.I. No. 610 of 2010). Soils at soil P Index 4 show
82 no agronomic response to P applications and have a higher risk of P loss in runoff (Tunney,
83 2000). Phosphorus losses from such a high P Index soil have the potential to become
84 exported along the nutrient transfer continuum within a catchment, and may adversely affect
85 water quality (Wall et al., 2011).

86

87 Pig farming in Ireland is concentrated in a small number of counties, with 52% of the
88 national sow herd located in counties Cavan, Cork and Tipperary (Anon, 2008). At 3.5 ha per
89 sow, the density of pig farming in County Cavan is the densest in the country (Anon, 2008).
90 Due to the high concentrations of pig farming in certain areas, the constant application of pig
91 slurry results in the local land becoming high in STP, which leads to an increased long-term
92 danger of P losses (which are known as chronic losses). In addition, due to regulations such
93 as S.I. No. 610 of 2010, the amount of slurry that may be spread on these lands will be
94 reduced, which will lead to a shortage of locally available land on which to spread slurry.

95

96 Alternative treatment methods for Irish pig slurry, such as constructed wetlands (CWs),
97 composting and anaerobic digestion (AD), were investigated by Nolan et al. (2012), but
98 landspreading was found to be the most cost effective treatment option. Land being used for
99 other farming practices, such as tillage, which may have a lower STP and would be more

100 suitable for the landspreading of slurry, is still often so far removed from the slurry source as
101 to make transportation of slurry to those locations extremely costly (Nolan et al., 2012).

102

103 A possible novel alternative, unexplored by Nolan et al. (2012), is the chemical amendment
104 of pig slurry. Based on a laboratory scale experiment, O'Flynn et al. (2012) suggested that
105 chemical amendment of pig slurry should be explored further, with flow dimensions added,
106 to examine nutrient speciation losses in runoff on a high P Index soil.

107

108 Alum, aluminium chloride (AlCl_3), lime and ferric chloride are commonly used as coagulants
109 in slurry and wastewater separation operations. Smith et al. (2004) found in a field-based
110 study that AlCl_3 , added at 0.75% of final slurry volume to slurry from pigs on a phytase-
111 amended diet, could reduce slurry dissolved reactive P (DRP) by 84% and runoff DRP by
112 73%. In a field study, Smith et al. (2001) found that alum and AlCl_3 , added at a
113 stoichiometric ratio of 0.5:1 Al: total phosphorus (TP) to pig slurry, achieved reductions of
114 33% and 45%, respectively, in runoff water, and reductions of 84% in runoff water when
115 adding both alum and AlCl_3 at 1:1 Al:TP. In an incubation study, Dou et al. (2003) found that
116 technical-grade alum, added to pig slurry at 0.25 kg kg^{-1} of slurry dry matter (DM), and flue
117 gas desulphurisation by-product (FGD), added at 0.15 kg kg^{-1} , each reduced DRP by 80%.
118 Dao (1999) amended stockpiled cattle manure with caliche, alum and flyash in an incubation
119 experiment, and reported water extractable P (WEP) reductions in amended manure,
120 compared to the study control, of 21, 60 and 85%, respectively.

121

122 O' Flynn et al. (2012) examined the effectiveness and feasibility of six different amendments,
123 added to pig slurry, at reducing DRP concentration in overlying water in an experiment
124 which attempted to simulate a contact mechanism between slurry and soil. Slurry and

125 amended slurry was applied to intact 100-mm-diameter soil cores, positioned in glass
126 beakers. The slurry was left for 24 h and the soil was gently saturated over a further 24 h. 500
127 mL of water was then added to the beaker. A rectangular paddle, positioned at mid-height in
128 the overlying water, was set to rotate at 20 rpm for 30 h to simulate overland flow, and water
129 samples were taken over the duration of the study and tested for DRP. The effectiveness of
130 the amendments at reducing DRP in overlying water were (in decreasing order): alum (86%),
131 FGD (74%), poly-aluminium chloride (PAC) (73%), ferric chloride (71%), flyash (58%)
132 and lime (54%). Ranked in terms of feasibility, which took into account effectiveness, cost
133 and other potential impediments to use, they were: alum, ferric chloride, PAC, flyash, lime
134 and FGD.

135

136 However, whilst allowing comparison between different amendments at reducing P in
137 overlying water, the agitator test did not simulate surface runoff of nutrients under conditions
138 which attempted to replicate on-farm scenarios. In the present study, a laboratory runoff box
139 study was chosen over a field study as it was less expensive and conditions such as surface
140 slope, soil conditions, and rainfall intensity can be standardized for testing. The expensive
141 nature of field experiments and inherent variability in natural rainfall has made rainfall
142 simulators a widely used tool in P transport research (Hart et al., 2004). The runoff-box
143 experiment was sufficient to compare treatments and no effort was made to extrapolate field-
144 scale coefficients using this experiment. Unlike previous studies, which used a much higher
145 rainfall intensity of 50 mm h⁻¹ (Smith et al., 2001; Smith et al., 2004), the present study
146 examined surface runoff of nutrients under a calibrated rainfall intensity of 10.3±0.15 mm h
147⁻¹, which has a much shorter return period and is more common in North Western Europe. It is
148 also high enough so as to produce runoff in a reasonable period of time. The present study

149 provides the first comparison of the effects on runoff concentrations and loads following the
150 addition of amendments to Irish pig slurry.

151

152 The aim of this laboratory study was to investigate P and suspended sediment (SS) losses
153 during three consecutive simulated rainfall events and to:

- 154 1) elucidate if amendment of pig slurry can control incidental (losses which take place
155 when a rainfall event occurs shortly after slurry application and before slurry infiltrates
156 into the soil) and chronic P losses over time to below that of the soil control, and
- 157 2) compare how amendment of pig slurry affects P speciation and metal losses in runoff
158 when compared with control and slurry only treatments.

159

160 **2. Materials and Methods**

161

162 **2.1. Slurry collection and characterisation**

163

164 Pig slurry was taken from an integrated pig unit in Teagasc Research Centre, Moorepark,
165 Fermoy, Co. Cork in March 2011. The sampling point was a valve on an outflow pipe
166 between two holding tanks, which were sequentially placed after a holding tank under the
167 slats. To ensure a representative sample, this valve was turned on and left to run for a few
168 minutes before taking a sample. The slurry was stored in a 25-L drum inside a fridge at 4°C
169 prior to testing. The TP and total nitrogen (TN) were determined using persulfate digestion.
170 Ammonium-N (NH₄-N) was determined by adding 50 mL of slurry to 1L of 0. 1M HCl,
171 shaking for 30 min at 200 rpm, filtering through No. 2 Whatman filter paper, and analysing
172 using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Slurry pH was
173 determined using a pH probe (WTW, Germany). Dry matter (DM) content was determined

174 by drying at 105°C for 24 h. The physical and chemical characteristics of the pig slurry used
175 in this experiment and characteristic values of pig slurry from other farms in Ireland are
176 presented in Table 2.

177

178 **2.2. Soil collection and analysis**

179

180 120-cm long, 30-cm wide, 10-cm deep intact grassed soil samples (n= 15) were collected
181 from a local dry stock farm in Galway, Republic of Ireland. Soil samples (n=3) – taken from
182 the upper 100 mm from the same location - were air dried at 40 °C for 72 h, crushed to pass a
183 2 mm sieve and analysed for Morgan’s P (the national test used for the determination of plant
184 available P in Ireland) using Morgan’s extracting solution (Morgan, 1941). Soil pH (n=3) was
185 determined using a pH probe and a 2:1 ratio of deionised water-to-soil. The particle size
186 distribution was determined using a sieving and pipette method (British Standard (B.S.)
187 1377-2; BSI, 1 990a) and the organic content of the soil was determined using the loss on
188 ignition (LOI) test (B.S.1377-3; BSI, 1990b). The soil used was a poorly-drained, sandy loam
189 textured topsoil (58% sand, 27% silt, 15% clay) with a STP of 16.72±3.58 mg L⁻¹ (making it
190 a P index 4 soil according to S.I. No. 610 of 2010, on which P may not be spread, except in
191 those circumstances mentioned in Table 1), total potassium (TK) of 127.39±14.94 mg L⁻¹, a
192 pH of 7.65±0.06 and an organic matter content of 13±0.1%.

193

194 **2.3. Slurry amendment**

195

196 The results of a laboratory micro-scale study by O’ Flynn et al. (2012) were used to select
197 amendments and their application rates to be used in the present study. The amendments,
198 which were applied on a stoichiometric basis, were: (1) commercial grade liquid alum (8%

199 Al₂O₃) applied at a rate of 0.88:1 [Al:TP]; (2) commercial-grade liquid ferric chloride (38%
200 FeCl₃) applied at a rate of 0.89:1 [Fe:TP]; and (3) commercial-grade liquid poly-aluminium
201 chloride (PAC) (10 % Al₂O₃) applied at a rate of 0.72:1 [Al:TP]. The other amendments used
202 in the O' Flynn et al. (2012) study (FGD, flyash and lime) were unexamined in the present
203 study on the basis of effectiveness and feasibility. The amendments were added to the slurry
204 in a 2-L plastic container, mixed for 10 s, and then applied evenly to the grassed sods. The
205 compositions of the amendments used are shown in Table 3.

206

207 **2.4. Rainfall simulation study**

208

209 100 cm-long, 22.5 cm-wide and 7.5 cm-deep laboratory runoff boxes, with side-walls 2.5 cm
210 higher than the grassed sods, were used in this experiment. The runoff boxes were positioned
211 under a rainfall simulator. The rainfall simulator consisted of a single 1/4HH-SS 14SQW
212 nozzle (Spraying Systems Co., Wheaton, IL) attached to a 4.5-m-high metal frame, and
213 calibrated to achieve an intensity of $10.3 \pm 0.15 \text{ mm h}^{-1}$ and a droplet impact energy of 260 kJ
214 $\text{mm}^{-1} \text{ ha}^{-1}$ at 85 % uniformity after Regan et al. (2010). The source for the water used in the
215 rainfall simulations had a DRP concentration of less than 0.005 mg L^{-1} , a pH of 7.7 ± 0.2 and
216 an electrical conductivity (EC) of 0.43 5 dS m^{-1} . Each runoff box had 5-mm-diameter
217 drainage holes located at 300-mm-centres in the base, after Regan et al. (2010). Muslin cloth
218 was placed at the base of each runoff box before packing the sods to prevent soil loss.
219 Immediately prior to the start of each experiment, the sods were trimmed and packed in the
220 runoff boxes. The packed sods were then saturated using a rotating disc, variable-intensity
221 rainfall simulator (after Williams et al., 1997), and left to drain for 24 h by opening the 5-
222 mm-diameter drainage holes before continuing with the experiment. At this point ($t = 24 \text{ h}$),
223 when the soil was at approximately field capacity, slurry and amended slurry were spread on

224 the packed sods and the drainage holes were sealed. They remained sealed for the duration of
225 the experiment. They were then left for 48 h in accordance with S.I. No. 610 of 2010 At t =
226 72 h, 96 h and 120 h (Rainfall Event (RE) 1, RE 2 and RE 3), rainfall was applied (to the
227 same sods), and each event lasted for a duration of 30 min after runoff began. Surface runoff
228 samples for each event were collected in 5-min intervals over this 30-min period. The
229 laboratory runoff box experiment was sufficient to compare treatments and no effort was
230 made to extrapolate field-scale coefficients using this experiment.

231

232 **2.5. Runoff collection and analysis**

233

234 The following treatments were examined in triplicate (n=3) within 21 d of sample collection:
235 (1) a grassed sod-only treatment with no slurry applied (2) a grassed sod with unamended
236 slurry (the slurry control) applied at a rate of 19 kg TP ha⁻¹, and (3) grassed sods receiving
237 amended slurry applied at a rate of 19 kg TP ha⁻¹.

238

239 After each 5-min interval, runoff water samples were tested for pH. A subsample was passed
240 through a 0.45 µm filter and analysed colorimetrically for DRP using a nutrient analyser
241 (Konelab 20, Thermo Clinical Labsystems, Finland). Filtered (passed through a 0.45 µm
242 filter) and unfiltered subsamples, collected at 10, 20 and 30 min after runoff began, were
243 tested for total dissolved phosphorus (TDP) and TP using acid persulfate digestion.

244 Particulate phosphorus was calculated by subtracting TDP from TP. Dissolved un-reactive
245 phosphorus was calculated by subtracting DRP from TDP. Suspended sediment was tested by
246 vacuum filtration of a well-mixed (previously unfiltered) subsample through Whatman GF/C
247 (pore size: 1.2 µm) filter paper. As the amendments used contain metals, namely Al and Fe,
248 filtered subsamples collected at 10, 20 and 30 min after runoff began, were analysed using an

249 ICP (inductively coupled plasma) VISTA-MPX (Varian, California). The limit of detection
250 was 0.01 mg L⁻¹.

251

252 **2.6. Statistical analysis**

253

254 This experiment analysed the pairwise comparisons of the mean concentrations of DRP,
255 DUP, TDP, PP, TP, SS, Al and Fe in the runoff when slurry only (slurry control), no slurry,
256 and slurry that was treated with alum, PAC and FeCl₃, was applied. The significances of the
257 pairwise comparisons were based upon the results of an analysis of the data by a multivariate
258 linear model in SPSS 19 (IBM, 2011). Covariance structures and interactions were
259 investigated, but found not to be of significance with respect to the pairwise comparisons.
260 Probability values of $p > 0.05$ were deemed not to be significant.

261

262 **3. Results and Discussion**

263

264 **3.1. Phosphorus in runoff**

265

266 The vast majority of the Irish landscape has rolling topography and is highly dissected with
267 surface water or drainage systems. The present laboratory experiment mimics a field
268 neighboring such a landscape. The high drainage density, high annual rainfall and low annual
269 potential evapotranspiration (20–50% of rainfall) facilitates the hydrological pathways for
270 transfers of P (Wall et al., 2011). However, the losses from the runoff boxes in the present
271 study may be buffered further before reaching this export continuum.

272

273 The flow weighted mean concentrations (FWMC) of P in runoff from the soil-only treatment
274 were constant for all REs, with TP and TDP decreasing from 0.62 and 0.42 mg L⁻¹
275 (corresponding to loads of 3.6 and 2.5 mg m⁻²), respectively, during RE 1 to 0.60 and 0.41
276 mg L⁻¹ (3.4 and 2.3 mg m⁻²) during RE 3 (Fig. 1). These concentrations of TP were above
277 0.03 mg P L⁻¹, the median phosphate level above which significant deterioration in water
278 quality may be seen in rivers (Clabby et al., 2008). These high losses were as expected as the
279 soil used was a P index 4 soil, which carries the risk of increased P loss in runoff (Tunney,
280 2000) and may not normally have P spread on it (S.I. No. 610 of 2010). Although the
281 buffering capacity of water ensures that the concentration of the water in a stream or lake will
282 not be as high as the concentration of runoff, chronic losses of P are a major issue in water
283 quality.

284

285 Phosphorus losses of all types increased with slurry application (Fig. 1). The FWMC of DRP
286 for the runoff from the slurry control, averaged over the three rainfall events, was 0.89 mg L⁻¹
287 (4.47 mg m⁻²), which was significantly different to, and over twice as high as the soil-only
288 treatment (p=0.00) (Table 4). Although the concentration of TDP in runoff from the slurry
289 control decreased slightly during each event (Fig. 1), the TDP fraction of TP increased from
290 45% during RE1 to 55% during RE2, and 66% during RE3. This was due to the level of PP in
291 runoff reducing, albeit not significantly (p>0.05), between each event. A similar trend was
292 replicated across all amended slurry treatments. As PP is generally bound to the minerals
293 (particularly Fe, Al, and Ca) and organic compounds contained in soil, and constitutes a long-
294 term P reserve of low bioavailability (Regan et al., 2010), it may provide a variable, but long-
295 term, source of P in lakes as it is associated with sediment and organic material in agricultural
296 runoff (Sharpley et al., 1992). The average FWMC of 0.89 mg DRP L⁻¹ (4.47 mg m⁻²) from
297 the slurry control was consistent with the results of Smith et al. (2001), who obtained DRP

298 concentrations of 5.5 mg L^{-1} in surface runoff following slurry application to grassland at
299 $44.9 \text{ kg TP ha}^{-1}$ and subjected to a rainfall intensity of 50 mm h^{-1} , 1 day after application.
300

301 Poly-aluminium chloride was the best performing amendment, and significantly reduced all P
302 to concentrations not significantly different ($p>0.05$) to soil-only. Across all treatments, no
303 form of P changed significantly between REs ($p>0.05$). Within each treatment and each
304 event, there were certain variances between replications expressed as standard deviations
305 from the average. These may be attributable to the inherent variability within soils and slurry,
306 such as differing chemical and physical properties, from two very non-homogeneous
307 materials.

308

309 The amendments used in this study all significantly reduced DRP, DUP, TDP, PP and TP
310 concentrations in the runoff water compared to the slurry control, but resulted in DRP
311 concentrations which were not significantly different ($p>0.05$) to the soil-only treatment. No
312 statistical relationship was found between the runoff P concentrations and pH, or volume of
313 runoff water measured during each test. Dissolved un-reactive phosphorus concentrations
314 from all amendments were not significantly different to each other ($p>0.05$) and were
315 significantly higher than the soil-only, but lower than the slurry control. Similarly, the
316 addition of amendments reduced the PP, TP and TDP losses below the slurry control (Table
317 4); however, they were still higher than the soil-only. This indicates that even after chemical
318 amendment, slurry spread on high STP soil still poses an environmental danger. This is
319 because chemical amendment of slurry will only affect the contribution of the slurry to runoff
320 P, but will not affect the contribution of the soil itself which, for high STP soils, may still
321 pose the danger of chronic P losses.

322

323 The average FWMC of DRP and TDP in runoff from the amended slurry treatments were
324 approximately half than in the runoff from the slurry control. This may be due to the
325 amendments reducing the DRP of the slurry itself, similar to what Smith et al. (2001)
326 experienced. Smith et al. (2001) added alum and AlCl₃, each at 0.5:1 and 1:1 Al:TP, to pig
327 slurry. Each reduced DRP in pig slurry by roughly 77% at 0.5:1 and 99% at 1:1. At the low
328 rate of application (0.5:1), DRP in runoff water was reduced by 33 and 45% when adding
329 alum and AlCl₃, respectively. At the high rate of application (1:1), each amendment reduced
330 runoff DRP by 84%. These were similar to the results obtained from the present study, which
331 ranged from 63% for alum added at 0.88:1 Al:TP to 71% for PAC added at 0.72:1 (Table 4).
332

333 **3.2. Suspended sediment, metals and pH in runoff**

334

335 The SS concentration in runoff reduced during each RE, apart from the soil-only treatment,
336 which was more constant. The amendments all reduced the SS concentration to below that of
337 the slurry control (Fig. 2) and, in the case of FeCl₃ and PAC, the average FWMC was below
338 35 mg L⁻¹, the treatment standard necessary for discharge to receiving waters (S.I. No 419 of
339 1994). However, the concentration of SS in the soil-only treatment and the slurry control
340 were highly variable. The SS concentrations in runoff were not significantly different
341 between treatments, apart from PAC, which was significantly different to the slurry control
342 (p=0.024).

343

344 The order of effectiveness of removal was the same as for P, i.e. from best to worst, they are:
345 PAC, FeCl₃ and alum. The removals of SS for alum (39 %), FeCl₃ (66 %) and PAC (74 %)
346 were not as high as those reported by Brennan et al. (2011), who reported SS removals of
347 88%, 65% and 83% in runoff when adding alum, FeCl₃ and PAC, respectively, to dairy cattle

348 slurry. However, the DM of the dairy cattle slurry used by Brennan et al. (2011) was 10.5%,
349 compared to 3.41% in this study, and all treatments resulted in average FWMCs well above
350 the slurry only treatment of the present study.

351

352 Figure 3 shows the average FWMCs of Al and Fe in runoff water. As expected, alum and
353 PAC resulted in increased levels of Al, with Al levels in runoff from alum significantly
354 different to all other treatments ($p < 0.05$). This agrees with Edwards et al. (1999), who
355 reported increased levels of Al in runoff water from alum-amended horse manure and
356 municipal sludge, compared to the slurry control, in a plot study. Edwards et al. (1999) added
357 alum at 10% by dry manure and dry sludge mass. Horse manure and municipal sludge were
358 spread at 9.3 and 7.8 Mg ha⁻¹, respectively, with rainfall applied within 1 h of application at
359 64 mm h⁻¹ for 30 min after runoff began. The FWMC of Al in runoff increased from 1.22
360 and 0.61 mg L⁻¹ from unamended horse manure and municipal sludge, respectively, to 1.80
361 and 1.01 mg L⁻¹ for alum-amended horse manure and municipal sludge. In the present study,
362 Al from PAC was significantly lower than from alum ($p = 0.00$), significantly higher than from
363 FeCl₃ ($p = 0.036$), but not significantly different to the soil-only or slurry control ($p > 0.05$).
364 FeCl₃ resulted in increased levels of Fe, significantly different ($p < 0.05$) to all other
365 treatments. Alum reduced Fe levels in runoff compared to the slurry control. This result was
366 in agreement with Moore et al. (1998) and Edwards et al. (1999). Moore et al. (1998) added
367 alum at 10% by weight in a plot study to poultry litter, which was spread at varying land
368 application rates up to 8.98 Mg ha⁻¹. Rainfall was applied immediately after slurry application
369 (RE1), and 7 days later (RE2) at 50 mm h⁻¹ for 27.5 min after runoff began. At the highest
370 land application rate, Fe loads in runoff were reduced from 94.2 and 31.1 g ha⁻¹ from the
371 slurry control for RE1 and RE2 to 37.8 and 12.1 g ha⁻¹ from the alum-amended litter.
372 Edwards et al. (1999) reported a FWMC of 0.17 mg Fe L⁻¹ in runoff from alum-amended

373 horse manure, compared to 0.44 mg L⁻¹ from unamended slurry, and 0.10 from soil-only.
374 There are no limits for levels of Al in surface water intended for the abstraction of drinking
375 water, but the concentrations of Fe measured in the runoff were well within the mandatory
376 limit of 0.3 mg L⁻¹(EEC, 1975).

377

378 The effect of amendments on slurry pH is a potential barrier to their implementation as it
379 affects P sorbing ability (Penn et al., 2011) and ammonia (NH₃) emissions from slurry
380 (Lefcourt and Messinger, 2001). The use of acidifying amendments can lead to an increased
381 release of hydrogen sulphide gas (H₂S) from slurry, which is believed to be responsible for
382 human and animal deaths when slurry is agitated on farms. However, the results from this
383 laboratory experiment showed the pH of the runoff water not to be significantly affected by
384 the use of amendments (p>0.05). However, further investigation would need to be undertaken
385 to confirm that pollution swapping (the increase in one pollutant as a result of a measure
386 introduced to reduce another pollutant (Healy et al., 2012)) does not occur.

387

388 **3.3. Outlook for use of amendments as a mitigation measure**

389

390 In this laboratory study, amendments to pig slurry significantly reduced runoff P from runoff
391 boxes compared to the slurry control. However, the DRP concentration in runoff remained at
392 or above the DRP concentration in runoff from soil only, indicating that, although incidental
393 losses can be mitigated by chemical amendment, chronic losses cannot be reduced. Future
394 research must examine the effect of amendments on P loss to runoff at field-scale under real-
395 life conditions with conditions which laboratory testing cannot mimic, such as the presence of
396 drainage, flow dynamics and a watertable. Other research which must also be carried out
397 includes the effect of amendments on leachate, gaseous emissions and plant available P.

398

399 The use of amendments also incurs the extra cost of purchasing amendments. O' Flynn et al.
400 (2012) estimated that the cost of spreading amended slurry at the stoichiometric rates used in
401 this study would be 3.33, 2.45, and 3.69 € m⁻³ for alum, FeCl₃ and PAC, respectively. This
402 would be in comparison to 1.56 € m⁻³ to spread unamended slurry.

403

404 Increased regulation of pig slurry management will accentuate the problem of chronic P
405 losses. A possible solution, unexamined in the present study, would be to modify the soil with
406 a P sorbing material.

407

408 **4. Conclusions**

409

410 The findings of this study were:

- 411 1. On the high soil test phosphorus soil tested, phosphorus losses from the grassed soil
412 only were high and were further increased following slurry application. All
413 amendments tested reduced all types of phosphorus losses, but did not reduce them
414 significantly to below that of the soil-only treatment, the average flow-weighted mean
415 concentration of total phosphorus of which was 0.61 mg L⁻¹ and which comprised
416 31% as particulate phosphorus. For the slurry control, the average flow weighted
417 mean concentration of the surface runoff was 2.17 mg total phosphorus L⁻¹, 47% of
418 which was particulate phosphorus. In decreasing order of effectiveness at removal of
419 phosphorus, the most successful amendments were: commercial-grade liquid poly-
420 aluminium chloride, which reduced the average flow weighted mean concentration of
421 total phosphorus to 0.64 mg L⁻¹ (42% particulate phosphorus); commercial-grade
422 liquid ferric chloride, which reduced total phosphorus to 0.91 mg L⁻¹ (52% particulate

423 phosphorus); and alum, which reduced total phosphorus to 1.08 mg L^{-1} (56%
424 particulate phosphorus).

425 2. For each treatment, total phosphorus and total dissolved phosphorus concentrations in
426 runoff decreased after each rainfall event. However, the fraction of total dissolved
427 phosphorus within runoff increased, due to large, although not significant, decreases
428 in particulate phosphorus between events.

429 3. The amendments all reduced the suspended sediment to below that of the slurry
430 control, and in the case of commercial-grade liquid ferric chloride and commercial-
431 grade liquid poly-aluminium chloride, to below that of the soil only. These two
432 treatments also reduced the average flow weighted mean concentration of suspended
433 sediment to below 35 mg L^{-1} , the treatment standard necessary for discharge to
434 receiving waters.

435 4. Although encouraging, the effectiveness of the amendments trialed in this study
436 should be validated at field scale.

437 **Acknowledgements**

438

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440 IRCSET to support this study. The authors would like to thank Dr. Raymond Brennan and
441 Liam Henry.

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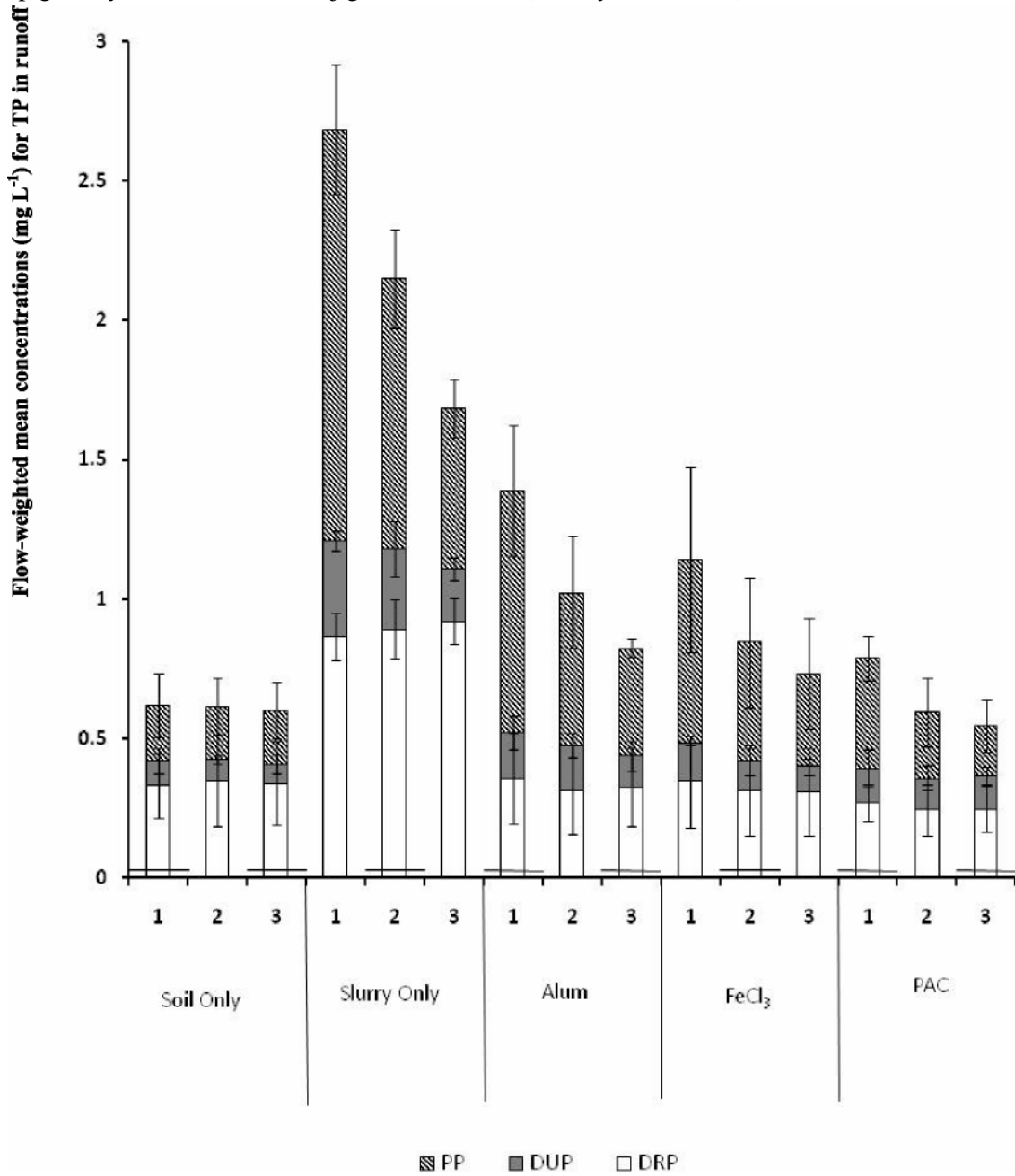
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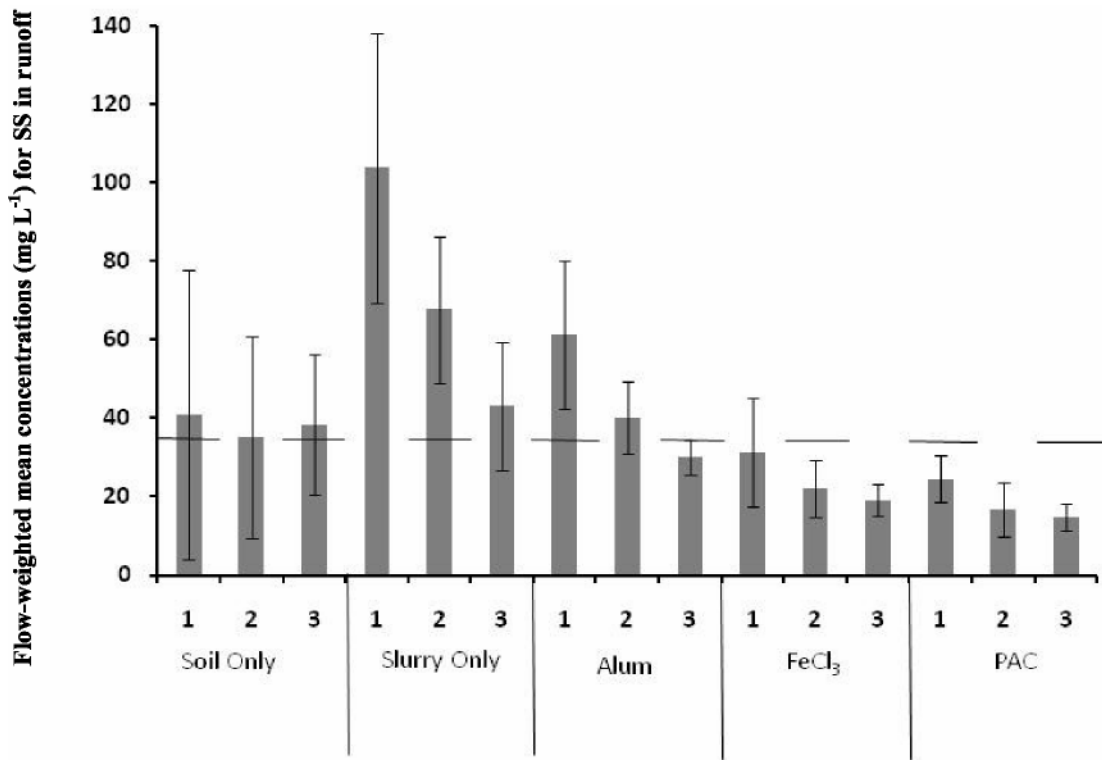
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597 Fig. 1. Histogram of flow-weighted mean concentrations (mg L^{-1}) for dissolved reactive
 598 phosphorus (DRP), dissolved unreactive phosphorus (DUP) and particulate phosphorus (PP)
 599 in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of
 600 pig slurry. Hatched line = 30 jig P L^{-1} standard (Clabby et al., 2008).



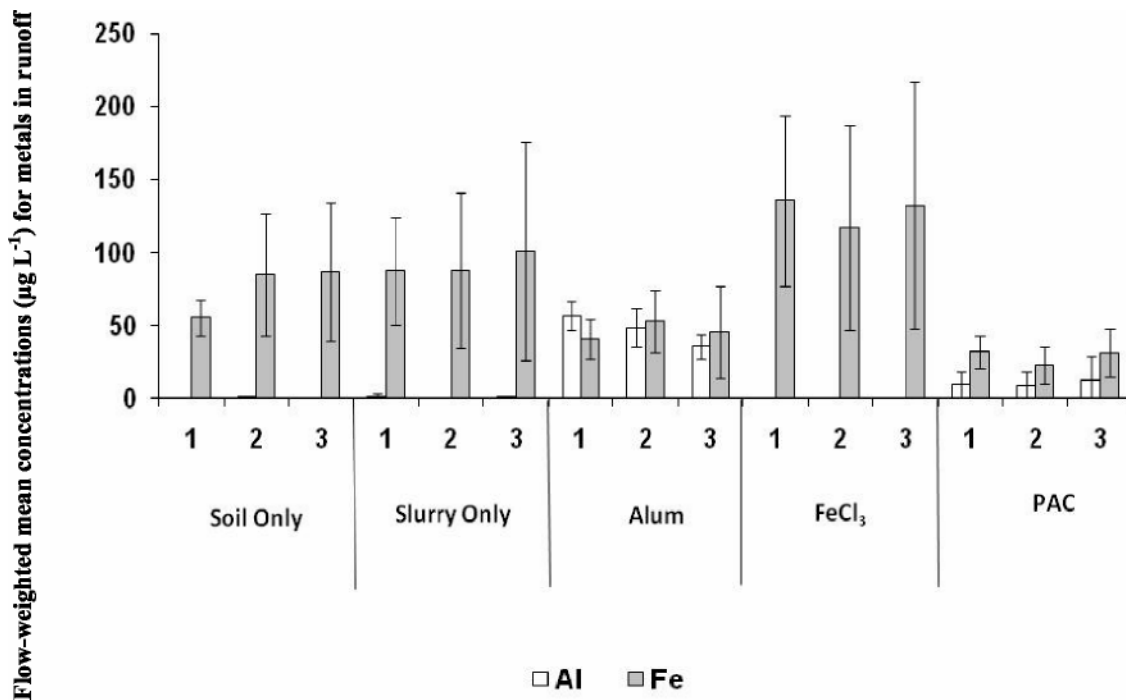
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606 Fig. 2. Histogram of average flow-weighted mean concentration of suspended sediment (SS)
 607 (mg L⁻¹) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land
 608 application of pig slurry. Hatched line = 35 mg L⁻¹ standard (S.I. No 419 of 1994).
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628 Fig. 3. Histogram of average flow-weighted mean concentration of metals (mg L^{-1}) in runoff
 629 at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig
 630 slurry.
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645 Table 1. Amount by which regulations may be exceeded over time.

Date	Amount by which regulations can be exceeded
	(kg P ha ⁻¹)
To January 1, 2013 ^a	Not limited
January 1, 2013 - January 1, 2015	5
January 1, 2015 - January 1, 2017	3
January 1, 2017 onwards	0

^aUp to 1 January 2013, the regulation limits can be exceeded when spreading spent mushroom compost, poultry manure, or pig slurry (Anon 2010, www.teagasc.ie). This can only happen if the activities which produce this on a holding have not increased in scale since 1 August 2006, and the N application limit is not exceeded (S.I. No. 610 of 2010).

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664 Table 2. Physical and chemical characteristics of the pig slurry used in this experiment and characteristic values of pig slurry from other farms in Ireland.

TP	TN	TK	NH ₄ -N	pH	DM	Reference
(mg L ⁻¹)					(%)	
613±40	2800±212		2290 ±39	7.85 ± 0.03	3.41± 0.08	The present study
800	4200					S.I. No. 610 of 2010
1630	6621	2666			5.77	McCutcheon, 1997 ^a
900±7	4600±21	2600±10			3.2±2.3	O' Bric, 1991 ^a

^aValues changed to mg L⁻¹ assuming densities of 1 kg L⁻¹, ± standard deviation

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Amendment		Alum	Ferric Chloride	PAC
		8% Al ₂ O ₃	38% FeCl ₃	10 % Al ₂ O ₃
pH		1.25		1.0 – 3.0
WEP	mg kg ⁻¹	0		
Al		4.23		
Ca				
Fe	%	<0.01	38	
K				
As		1	<2.8	<1.0
Cd		0.21	<3.4	<0.2
Co				
Cr		2.1	<48	<2.0
Cu			<65	
Mg				
Mn			<1370	
Mo				
Na				
Ni	mg kg ⁻¹	1.4	<48	<1.0
P				
Pb		2.8	<14	<2.0
V				
Zn				
Sb			<2.8	<1.0
Se			<2.8	<1.0
Hg			<0.7	<0.2

692 Table 4. Flow-weighted mean concentrations (mg L^{-1}) averaged over three rainfall events, and removals (%) for dissolved reactive P (DRP),
 693 dissolved un-reactive P (DUP), total dissolved P (TDP), particulate P (PP), total P (TP), and suspended sediment (SS).

	DRP	Removal	DUP	Removal	TDP	Removal	PP	Removal	TP	Removal	SS	Removal
	mgL^{-1}	%	mgL^{-1}	%	mgL^{-1}	%	mgL^{-1}	%	mgL^{-1}	%	mgL^{-1}	%
Soil Only	0.34 ^{ab}	-	0.08 ^a	-	0.42 ^a	-	0.19 ^a	-	0.61 ^a	-	38.06 ^{ab}	-
Slurry Only	0.89 ^c	-	0.27 ^b	-	1.17 ^b	-	1.01 ^b	-	2.17 ^b	-	71.52 ^b	-
Alum	0.33 ^a	63	0.15 ^c	46	0.48 ^a	59	0.60 ^{cd}	40	1.08 ^{cd}	50	43.82 ^{ab}	39
FeCl ₃	0.32 ^b	64	0.11 ^c	59	0.43 ^c	63	0.47 ^c	53	0.91 ^c	58	24.27 ^{ab}	66
PAC	0.26 ^{ab}	71	0.12 ^c	56	0.37 ^{ac}	68	0.27 ^{ad}	73	0.64 ^{ad}	70	18.61 ^a	74

abcd Means in a column, which do not share a superscript, were significantly different ($P < 0.05$)

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