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7 **Impact of chemical amendment of dairy cattle slurry on phosphorus, suspended sediment**
8 **and metal loss to runoff from a grassland soil.**
9

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12 R.B. Brennan¹, O. Fenton², J. Grant³, M.G. Healy^{1*}
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16

17 ¹Civil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of Ireland.

18 ²Teagasc, Johnstown Castle, Environmental Research Centre, Co Wexford, Rep. of Ireland

19 ³Teagasc Research Centre, Kinsealy, Co. Dublin.
20

21 Corresponding author. Tel: +353 91 495364; fax: +353 91 494507. E-mail address:

22 mark.healy@nuigalway.ie
23
24
25

26 **Abstract**

27

28 Emerging remediation technologies such as chemical amendment of dairy cattle slurry have the
29 potential to reduce phosphorus (P) solubility and consequently reduce P losses arising from land
30 application of dairy cattle slurry. The aim of this study was to determine the effectiveness of
31 chemical amendment of slurry to reduce incidental losses of P and suspended sediment (SS)
32 from grassland following application of dairy cattle slurry and to examine the effect of
33 amendments on metal concentrations in runoff water. Intact grassed-soil samples were placed in
34 two laboratory runoff boxes, each 200-cm-long by 22.5-cm-wide by 5-cm-deep, before being
35 amended with dairy cattle slurry (the study control) and slurry amended with either: (i) alum,
36 comprising 8% aluminium oxide (Al_2O_3) (1.11:1 aluminum (Al):total phosphorus (TP) of slurry)
37 (ii) poly-aluminum chloride hydroxide (PAC) comprising 10% Al_2O_3 (0.93:1 Al:TP) (iii)
38 analytical grade ferric chloride (FeCl_2) (2:1 Fe:TP), (iv) and lime ($\text{Ca}(\text{OH})_2$) (10:1 Ca:TP). When
39 compared with the study control, PAC was the most effective amendment, reducing dissolved
40 reactive phosphorus (DRP) by up to 86% while alum was most effective in reducing SS (88%),
41 TP (94%), particulate phosphorus (PP) (95%), total dissolved phosphorus (TDP) (81%), and
42 dissolved unreactive phosphorus (DUP) (86%). Chemical amendment of slurry did not appear to
43 significantly increase losses of Al and Fe compared to the study control, while all amendments
44 increased Ca loss compared to control and grass-only treatment. While chemical amendments
45 were effective, the reductions in incidental P losses observed in this study were similar to those
46 observed in other studies where the time from slurry application to the first rainfall event was
47 increased. Timing of slurry application may therefore be a much more feasible way to reduce

48 incidental P losses. Future work must examine the long-term effects of amendments on P loss to
49 runoff and not only incidental losses.

50

51 *Keywords:* alum; poly-aluminium chloride; lime; ferric chloride; runoff; dairy; slurry;
52 management; grasslands

53

54 **Introduction**

55

56 Land application of dairy cattle slurry can result in incidental and chronic phosphorus (P) losses
57 to a waterbody (Buda et al., 2009), which may lead to eutrophication (Carpenter et al., 1998).

58 Incidental P losses take place when a rainfall event occurs shortly after slurry application and
59 before slurry infiltrates the soil, while chronic P losses are a long-term loss of P from soil as a
60 result of a build-up in soil test P (STP) caused by application of inorganic fertilisers and manure
61 (Buda et al., 2009). Incidental P losses arising from rainfall events following land application of
62 dairy cattle slurry are the focus of this study.

63

64 Withers et al. (2003) examined the results of a number of studies examining P losses following
65 land application of dairy cattle slurry at different rates and under different climatic conditions
66 (Smith et al., 2001a; Withers et al., 2001; Withers and Bailey, 2003) and found that incidental P
67 losses can account for between 50 and 90% of P losses from land to water. Suspended sediment
68 (SS) losses contribute to particulate phosphorus (PP) in runoff from tillage soils (Regan et al.,
69 2010); however, in grasslands most P loss is in dissolved form with total dissolved phosphorus
70 (TDP) and dissolved reactive phosphorus (DRP) comprising 69% and 60% of total phosphorus

71 (TP) load in surface runoff (Haygarth et al., 1998). Incidental SS losses following slurry
72 application can result in high concentrations of SS in runoff, resulting in increased PP losses
73 (Preedy et al., 2001; Withers et al., 2003). This PP can be mineralised and become available to
74 algae (Sharpley, 1993).

75

76 Mitigation methods to reduce incidental P losses include incorporating slurry into soil
77 immediately after land application (Tabbara, 2003), increasing length of buffer zones between
78 slurry application areas and drains and streams (Mayer et al, 2006), enhanced buffers strips
79 (Uusi-Kämppe et al., 2010), timing of slurry application (Hanrahan et al., 2009) and diet
80 manipulation (O'Rourke et al., 2010). The risk of P loss from slurry is strongly related to the
81 water extractable P (WEP) in the slurry (Dou et al., 2003) and amendments which reduce P
82 solubility should reduce P loss to runoff.

83

84 Chemical amendment of slurry using aluminium (Al), iron (Fe), or calcium (Ca) based
85 compounds reduce P solubility in manure (Dao, 1999; Dou et al., 2003; Kalbasi and
86 Karthikeyan, 2004) and reduce P in runoff from plots receiving alum amended poultry litter
87 (Moore and Edwards, 2005) with negligible effect on metal loss (McFarland et al., 2003).

88 Chemical amendments reduce incidental P losses by a combination of the formation of stable
89 metal-phosphorus precipitates (such as Al-P phosphates in the case of alum) and flocculation of
90 the particles in the slurry to form larger particles, which are less prone to erosion

91 (Tchobanoglous et al., 2003). Previous studies have found that there was no risk of increased
92 metal release posed by chemical amendment of poultry litter (Moore et al., 1998), dirty water

93 (McFarland et al., 2003), or horse manure (Edwards et al., 1999). The present study examines the

94 effect of chemical amendment of dairy cattle slurry on both P and metal (namely Al, Fe and Ca)
95 losses to runoff. Previous studies have only examined the effect of amendments on P solubility
96 (Dao, 1999; Dao and Daniel, 2002; Dou et al., 2003).

97

98 Chemical amendments can be incorporated into soil to reduce soluble P in soils with high STP
99 (Novak and Watts, 2005), added directly to the manure before land application (Moore et al.,
100 1998), or applied after manure application to reduce P losses in runoff (Torbert et al., 2005).

101 Chemical amendment of poultry litter has been proven to be effective in reducing P losses from
102 poultry litter in the U.S.A. and has been used there for over 30 years (Moore and Edwards,
103 2005). However, there has been limited work involving chemical amendment of dairy manure
104 (Dao, 1999; Dou et al., 2003; Kalbasi and Karthikeyan, 2004). In an incubation study, Dou et al.
105 (2003) found that technical grade alum, added at 0.1 kg/kg (kg alum per kg slurry) and 0.25
106 kg/kg, reduced WEP in swine and dairy slurry by 80% and 99%, respectively. Dao (1999)
107 amended farm yard manure with caliche, alum and flyash in an incubation experiment, and
108 reported WEP reductions in amended manure compared to the control of 21, 60 and 85%,
109 respectively. Kalbasi and Karthikeyan (2004) applied untreated and amended dairy slurry to a
110 soil and incubated it for 2 years; alum and FeCl_2 were observed to decrease P solubility, while
111 lime amendments increased WEP.

112

113 The objectives of this study were to investigate (i) the effect of chemical amendments on
114 incidental losses of DRP, TDP, dissolved unreactive P (DUP), PP, TP and SS in runoff from a
115 grassed soil receiving dairy cattle slurry (the study control) or chemically amended dairy cattle

116 slurry in a laboratory rainfall simulator and (ii) the effect of amendments on metal concentrations
117 in runoff.

118

119 **2. Materials and Methods**

120

121 2.1. Soil sample collection and analysis

122

123 Intact grassed-soil samples, 70 cm-long by 30 cm-wide by 10 cm deep, were collected from a
124 dairy farm in Athenry, Co. Galway (53°21'N, 8°34' W). A second set of soil samples, taken to a
125 depth of 10 cm below the ground surface from the same location, were air dried at 40 °C for 72
126 h, crushed to pass a 2 mm sieve, and analysed for Morgan's P (the national test used for the
127 determination of plant available P in Ireland) using Morgan's extracting solution (Morgan,
128 1941). Soil pH (n=3) was determined using a pH probe and a 2:1 ratio of deionised water-to-soil.
129 Particle size distribution was determined using B.S.1377-2:1990 (BSI, 1990a). Organic content
130 of the soil was determined using the loss of ignition test (B.S.1377-3; BSI, 1990b). The soil was
131 a poorly-drained sandy loam (58% sand, 27% silt, 15% clay) with a Morgan's P of 22±3.9 mg P
132 L⁻¹, a pH of 7.45±0.15 and an organic matter (OM) content of 13±0.1%. The soil had a sandy
133 loam texture, which points to moderate drainage on site. However, medium permeable subsoil
134 limits drainage. Historic applications of organic P from an adjacent commercial-sized piggery
135 have led to high STP in the soil used in this study.

136

137 2.2. Slurry collection and analysis

138

139 Cattle slurry from dairy replacement heifers was taken from a farm (53°18' N, 8°47' W) in
140 County Galway, Republic of Ireland in Winter (February), 2010. The storage tanks were agitated
141 and slurry samples were transported to the laboratory in 10-L drums. Slurry samples were stored
142 at 4°C. Slurry and amended slurry pH was determined using a pH probe (WTW, Germany) and
143 the WEP of slurry was measured at the time of land application after Kleinman et al. (2007). Dry
144 matter (DM) content was determined by drying at 105 °C for 16 h. The TP of the dairy cattle
145 slurry was determined after Byrne (1979). Total potassium (TK), total nitrogen (TN) and TP
146 were carried out colorimetrically using an automatic flow-through unit (Varian Spectra 400
147 Atomic Absorption instrument). Ammoniacal nitrogen (NH₄-N) of slurry and amended slurry
148 was extracted from fresh slurry by shaking 10 g of slurry in 200 ml 0.1 M HCl on a peripheral
149 shaker for 1 h and filtering through No 2 Whatman filter paper.

150

151 2.3. Slurry amendment and runoff set-up

152

153 The results of a laboratory micro-scale study by Brennan et al. (2011) were used to select
154 chemical amendments to be examined in the present study. In addition to a grassed soil-only
155 treatment, five treatments were examined: (i) slurry-only (the study control), (ii) industrial grade
156 liquid alum (Al₂(SO₄)₃.nH₂O), comprising 8% aluminium oxide (Al₂O₃) applied at a rate of
157 1.11:1 (Al:TP) (iii) industrial grade liquid poly-aluminium chloride hydroxide (PAC)
158 (Al_n(OH)_mCl_{3n-m}) comprising 10% Al₂O₃ at a rate of 0.93:1 (Al:TP) (iv) analytical grade FeCl₂
159 at a rate of 2:1 (Fe:TP), and (v) burnt lime (Ca(OH)₂) at a rate of 10:1 (Ca:TP). The rates used
160 were based on the results Brennan et al. (2011).

161

162 A batch experiment was also conducted using a range of amendment concentrations to construct
163 a multi-point Langmuir isotherm (McBride, 2000):

$$164 \quad \frac{C_e}{\frac{x}{m}} = \frac{1}{ab} + \frac{C_e}{b} \quad (1)$$

165 where C_e is the concentration of P in solution at equilibrium (mg L^{-1}), x/m is the mass of P
166 adsorbed per unit mass of amendments (g kg^{-1}) at C_e , a is a constant related to the binding
167 strength of molecules onto the amendments, and b is the theoretical amount of P adsorbed to
168 form a complete monolayer on the surface. This provided an estimate of the maximum
169 adsorption capacity of the amendments (g kg^{-1}). The amendments were added at a range of rates
170 to 500 g slurry samples and mixed rapidly for 10 min at 100 rpm using a jar test flocculator. The
171 samples were incubated at 11°C for 24 h. Following incubation, 50 g of slurry/amended slurry
172 was mixed with 250 ml of distilled water. The slurry-water solution was then placed on a
173 reciprocating shaker for 1 h. Samples were centrifuged at 14,000 rpm for 5 min to separate the
174 solids from the solution before being passed through a $0.45 \mu\text{m}$ filter and the P extract was
175 determined using a Konelab nutrient analyser (Konelab 20, Thermo Clinical Labsystems,
176 Finland).

177

178 The equilibrium P concentration (EPC_0) (i.e. the point where no net desorption or sorption
179 occurs) was derived using the following formula (Olsen and Watanabe, 1957):

180

$$181 \quad S' = k_d C - S_0 \quad (2)$$

182

183 where S' is the mass of P adsorbed from slurry (mg kg^{-1}), C is the final P concentration of the
184 solution, k_d is the slope of the relationship between S' and C , and S_0 is the amount of P originally

185 sorbed to the amendment (mg L^{-1}). A slurry sample (from the same storage tank as used in the
186 surface runoff experiments) with a DM of 6%, TP of 550 mg L^{-1} and WEP of 2.26 g kg^{-1} was
187 used for the isotherm study. An approximate metal: soluble P ratio for each amendment was
188 calculated using the b term from the Langmuir isotherm and WEP of the slurry. These ratios
189 were equivalent to stoichiometric metal: TP ratios of 0.6:1 compared to 1.1:1 used in the present
190 study for alum and 1.5:1 compared to 0.93:1 for PAC and were generally in agreement with the
191 findings of Brennan et al. (2011), but were not in agreement for FeCl_2 (0.4:1 compared to 2:1)
192 and lime (0.9:1 compared to 10:1). The isotherm results indicated that lower application rates
193 should be sufficient to bind P in slurry. However, as the Brennan et al. (2011) study was
194 considered to best replicate surface runoff, it was decided to base the application rates on the
195 results of Brennan et al. (2011) and not the batch test used to develop the Langmuir isotherm. As
196 one of the main aims of the present study was to investigate the effect of amendments on metal
197 release, it was considered to be reasonable and conservative to use results from Brennan et al.
198 (2011). In the case of alum and PAC the rates used were approximately equal to 1:1 metal to TP
199 which was in agreement with Brennan et al (2011) and previous batch studies (Dao and Daniel,
200 2002). In the case of FeCl_2 the most efficient rate used in the Brennan et al (2011) study was
201 examined. When lime applied at 1:1 in Brennan et al (2011) study there was no effect; therefore
202 the results of Brennan et al (2011) study were used. As one of the main aims of the present study
203 was to investigate the effect of amendments on metal release, it was considered to be reasonable
204 and conservative to use results from Brennan et al. (2011).

205

206 A laboratory runoff box study was chosen over a field study as it was less expensive and allowed
207 testing under standardized conditions. Such studies are a widely used tool in P transport research

208 to compare treatments (Hart et al., 2004). This experiment used two laboratory runoff boxes,
209 200-cm-long by 22.5-cm-wide by 5-cm-deep with side walls 2.5 cm higher than the soil surface,
210 and 0.5-cm-diameter drainage holes located at 30-cm-centres in the base (after Regan et al.,
211 2010). Cheese cloth was placed at the base of each runoff box before placing the sods to prevent
212 soil loss. Intact grassed sods from the study site were transported to the laboratory and stored at
213 11°C in a cold room prior to testing. All experiments were carried out within 14 d of sample
214 collection and tests were conducted in triplicate (n=3). Immediately prior to the start of each
215 runoff box experiment, new sods were trimmed and placed in the runoff box; each slab was
216 butted against its adjacent slab to form a continuous surface. Molten candle wax was used to seal
217 any gaps between the soil and the sides of the runoff box, while the joint between adjacent soil
218 samples did not require molten wax.

219
220 The packed sods were then saturated using a rotating disc, variable-intensity rainfall simulator
221 (after Williams et al., 1997), comprising a single 1/4HH-SS14SQW nozzle (Spraying Systems
222 Co., Wheaton, IL) attached to a 450-cm-high metal frame, and calibrated to achieve an intensity
223 of $1.15 \pm 1 \text{ cm h}^{-1}$ and a droplet impact energy of $26 \text{ kJ cm}^{-1} \text{ ha}^{-1}$ at 85% uniformity. The sods
224 were then left to drain for 24 h before the experiment commenced; the grassed sods were then
225 assumed to be at an approximate 'field capacity' (Regan et al., 2010). Amendments were added
226 to the slurry and mixed rapidly (10 min at 100 rpm) using a jar test flocculator immediately prior
227 to land application. Slurry and amended slurry were applied directly to the surface of the intact
228 grassed soil in runoff boxes at a rate equivalent to $33 \text{ m}^3 \text{ slurry ha}^{-1}$ (26 kg TP ha^{-1}), the rate most
229 commonly used in Ireland (Coulter and Lalor, 2008). During each rainfall simulation event, rain
230 was applied until runoff water flowed continuously and then for 1 h while runoff water samples

231 were collected. The drainage holes on the base of the runoff boxes were sealed to better replicate
232 field conditions and to ensure that overland flow occurred. The first rainfall simulation (RS1)
233 commenced 48 h after slurry application, then after a 1 h interval the second rainfall simulation
234 (RS2) commenced. The drainage holes at the bottom of the runoff box were opened for a 24 h
235 interval and then closed when the third rainfall event (RS3) commenced. As the soil samples
236 were taken from the mid-slope of a field with a slope of approximately 5%, it would have been
237 unrealistic to allow the soil to remain water-logged for 24 h between RS2 and RS3. All of the
238 surface runoff was collected at 5-min intervals once runoff began. The source for the water used
239 in the rainfall simulations had a DRP concentration of less than 0.005 mg L^{-1} , a pH of 7.7 ± 0.2
240 and an electrical conductivity (EC) of 0.435 dS m^{-1} . Runoff water pH and EC were measured
241 immediately prior to each event using a pH and EC meter.

242

243 2.4. Sample handling and analysis

244

245 Runoff samples were collected in 1 L containers (covered to prevent rain water entering container)
246 at the bottom of the runoff box. Immediately after collection, a subsample of the runoff water
247 was passed through a $0.45 \mu\text{m}$ filter and a sub-sample was analysed colorimetrically for DRP
248 using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). A second filtered
249 sub-sample was analysed for TDP using potassium persulfate and sulfuric acid digestion (HACH
250 LANGE, Germany). Unfiltered runoff water samples were also collected and TP was measured
251 using the method used for TDP analysis. Particulate P was calculated by subtracting TDP from
252 TP. The DRP was subtracted from the TDP to give the DUP.

253

254 Suspended sediment were determined for all samples by vacuum filtration of well-mixed,
255 unfiltered runoff water through Whatman GF/C (pore size: 1.2 μm) filter paper. All water
256 samples were tested in accordance with standard methods for the examination of water and
257 wastewater (APHA, 2005). In order to address the concern of metal release from amendments,
258 identified by Fenton et al. (2008), it was decided to measure Al, Ca and Fe as these were the
259 active metals in the chemical amendments added to slurry. The metal content was determined
260 using an ICP (inductively coupled plasma) VISTA-MPX (Varian, California). The limit of
261 detection for Al and Fe was 0.01 mg L^{-1} and 1 mg L^{-1} for Ca.

262

263 2.5. Statistical analysis

264

265 The structure of the experiment was a one-way classification with the rainfall events being
266 repeated measures on each experimental unit. Proc Mixed of SAS (2004) was used to analyse the
267 concentrations of DRP, DUP, PP, TP, SS, Al, Ca and Fe with a covariance structure to account
268 for correlations between the repeated measures. An unstructured covariance model was used for
269 most variables and the outcome was interpreted as a factorial of treatment x event. In all cases,
270 the treatment by event interactions were examined. The data for Al and Fe were censored by a
271 limit of detection and PROC NLMIXED of SAS was used to fit a censored Normal-based model
272 while accounting for the correlations by inducing a compound symmetry structure with a random
273 effect.

274

275 **3. Results**

276

277 3.1. Slurry and amended slurry analysis

278

279 The results of the slurry analysis are shown in Table 1. The slurry sample was typical of slurry
280 found on farms in Ireland (Anon, 2010) with a high DM on the upper limit for land application
281 (Lalor, 2011 *per com*). The slurry TP and TK remained relatively constant. At the rates used in
282 this study, all of the amendments examined reduced the WEP of dairy cattle slurry by
283 approximately 99% compared to the slurry-control ($p < 0.001$). Alum addition reduced slurry pH
284 from approximately 7.5 (control) to 5.4, PAC reduced pH to 6.4 and FeCl_2 to 6.7 ($p < 0.001$),
285 while lime addition increased slurry pH to 12.2 ($p < 0.001$).

286

287 The results of the Langmuir isotherm are shown in Fig. 1. The binding strength of alum and PAC
288 was very high, followed by FeCl_2 and lime, which had the lowest binding strength of all
289 amendments examined. The EPC_0 was determined graphically for alum and PAC; however, as
290 lime and FeCl_2 were not in equilibrium, it was not possible to determine EPC_0 (Fig 2).

291

292 3.2. Water quality analysis

293

294 The average flow-weighted mean concentrations (FWMC) of DRP, DUP and PP in runoff for the
295 three rainfall events are shown in Fig. 3. Alum ($114 \mu\text{g DRP L}^{-1}$) and PAC ($89 \mu\text{g DRP L}^{-1}$) were
296 more effective at reducing DRP concentration than lime ($200 \mu\text{g DRP L}^{-1}$) and FeCl_2 ($200 \mu\text{g}$
297 DRP L^{-1}). There was no significant difference in DRP concentrations in the runoff from grass-
298 only and amended plots. At the rates used, all of the treatments examined resulted in DRP
299 concentrations in runoff greater than the maximum allowable concentration (MAC) of $30 \mu\text{g}$

300 DRP L⁻¹ for surface waters. However, the buffering capacity of water means that the
301 concentration of a surface waterbody will not be as high as the concentration of runoff, provided
302 runoff from slurry flows over soil which has not received dairy cattle slurry (McDowell and
303 Sharpley, 2002).

304
305 The average concentrations of P in runoff water for the 3 rainfall simulation events were 171 µg
306 DRP L⁻¹, 91 µg DUP L⁻¹ and 373 µg TP L⁻¹ for grassed soil-only treatment compared to 655 µg
307 DRP L⁻¹, 1,290 µg DUP L⁻¹ and 8,390 µg TP L⁻¹ for the slurry-control. Incidental DRP and TP
308 concentrations in runoff water following land application of dairy cattle slurry were 5 and 14
309 times greater than those from grassed-soil. In the present study, alum ($p<0.001$), PAC ($p<0.001$),
310 lime ($p<0.05$) and FeCl₂ ($p<0.05$) reduced DRP losses significantly compared to the slurry-
311 control with reductions similar to those observed in the Brennan et al. (2011) study. The results
312 of both studies are tabulated in Table 2. The average FWMC of TDP was significantly reduced
313 compared to the slurry-control. The difference between grass-only, alum and PAC treatments
314 was not significant and the difference between lime and FeCl₂ was also not significant. The
315 average FWMC of DUP was also significantly reduced for all treatments compared to slurry-
316 control.

317
318 There was no significant difference between TP in runoff water from grass-only (373 µg L⁻¹) and
319 alum treatments (506 µg L⁻¹). However, there was a significant difference between grass-only
320 and PAC (1,150 µg L⁻¹) ($p<0.001$), lime (1,270 µg L⁻¹) and FeCl₂ (2,400 µg L⁻¹) treatments for
321 TP ($p<0.001$), with a less significant difference between grass-only and PAC (790 µg L⁻¹) and
322 Fe (1,730 µg L⁻¹) for PP ($p<0.001$). Therefore, alum was the best amendment at reducing TP and

323 PP loss to runoff. Table 2 shows the TP lost in the runoff expressed as a percentage of the slurry
324 applied. The TP losses from control were in agreement with Preedy et al. (2001), who reported
325 that between 6 and 8% of TP applied was lost to runoff. The TP in runoff from the grass-only
326 treatment comprised approximately 47% DRP compared to 69% reported by Haygarth et al.
327 (1998). This difference may be a result of scale effects or differences in experiment design.
328 While chemical amendment of dairy slurry significantly reduced DRP, DUP, PP and TP in
329 runoff water, the proportions of each faction in runoff from alum, PAC and FeCl₂ treatments
330 were similar to slurry-control (Fig. 4).

331

332 Suspended sediment was 162 mg L⁻¹ for the grass-only treatment compared to 3,030 mg L⁻¹ for
333 the slurry-control (Fig. 5). The average FWMC of SS in runoff for the three rainfall events are
334 shown in Fig. 4. Alum resulted in the greatest reduction in SS (an average of 88% for the three
335 rainfall events compared to the slurry-control) ($p < 0.001$). There was no statistical difference in
336 average FWMC of SS between alum, PAC (83% reduction) and lime (82%). All of the
337 treatments resulted in SS concentrations in the runoff which were significantly greater than the
338 grass-only treatment ($p < 0.005$).

339

340 3.3. Metals in runoff water

341

342 The average FWMC of Al, Ca and Fe for the 3 rainfall simulation events are shown in Figs. 6, 7
343 and 8. The average concentrations of metals tested in runoff water for the 3 rainfall simulation
344 events were greater for the slurry-control than the grass-only treatment. Aluminium

345 concentrations increased from 60 to 91 $\mu\text{g Al L}^{-1}$ (not statistically significant), calcium from 84
346 to 108 mg Ca L^{-1} ($p < 0.01$), and Fe increased from 71 to 151 $\mu\text{g Fe L}^{-1}$ ($p = 0.02$, RS2).

347

348 The FWMC of Al decreased for all treatments compared to the slurry-control (Fig. 6). There was
349 a significant treatment x event interaction ($p < 0.001$) and differences between events within
350 treatments and between treatments within events were tested. After multiple comparison
351 adjustments, there were no statistically significant differences between treatments. There were
352 some significant decreases to the RS3 event compared to RS1 and RS2 for the lime and slurry-
353 control treatments ($p = 0.03$ and $p = 0.006$). The FWMC of Ca in runoff from all chemically
354 amended slurry treatments was significantly greater than from the slurry-control and the grass-
355 only treatment ($p < 0.01$) (Fig. 7).

356

357 The treatment x event interaction was significant and while no treatments were statistically
358 different across all events, there were some differences between the grass treatment and both
359 alum ($p = 0.02$, RS1) and the slurry-control ($p = 0.02$, RS2), and also between the FeCl_2 and slurry-
360 control ($p = 0.02$, RS2).

361

362 **4. Discussion**

363

364 4.1. Slurry and amended slurry analysis

365

366 The amendments examined significantly reduced WEP in amended slurry compared to the
367 control. This was in agreement with previous studies (Dao, 1999; Dou et al., 2003). Lefcourt and

368 Meisinger (2001) reported a 97% reduction in WEP of dairy cattle slurry when 2.5% by weight
369 of alum was added in a laboratory batch experiment. Dao and Daniel (2002) added alum (810 mg
370 Al L⁻¹) and ferric chloride (810 mg Fe L⁻¹) (compared to 1250 mg Al L⁻¹ and 2280 mg Fe L⁻¹ in
371 this study) to dairy slurry and observed that slurry WEP was reduced by 66 and 18%,
372 respectively. At higher application ratios of metal-to-TP, this study showed that greater
373 reductions in WEP are achievable.

374

375 The amendments also changed the pH of the slurry. Lime addition increased slurry pH
376 significantly, resulting in a 25 and 30% reduction in NH₄-N and TN of slurry following
377 amendment and mixing (Table 1). This was similar to findings of a study by Molloy and Tunney
378 (1983), who reported an increase in pH to 7.8 and a 50% increase in ammonia (NH₃) loss when
379 CaCl₂ was added to dairy slurry. This loss in NH₄-N was most likely due to NH₃ volatilisation,
380 as depending on the pH of a solution, NH₄-N can occur as NH₃ gas or the ammonium ion (NH₄)
381 (Gay and Knowlton, 2005). This reduces the fertiliser value of the slurry and increases NH₃
382 emissions from slurry. Addition of alum, PAC and FeCl₂ to dairy cattle slurry significantly
383 reduced pH, as expected. This phenomenon has been reported by a number of studies examining
384 the use of amendments to reduce NH₃ losses from dairy cattle slurry (Meisinger et al., 2001; Shi
385 et al., 2001). Meisinger et al. (2001) reported a 60% reduction in NH₃ loss from dairy cattle
386 slurry when 2.5% by weight of alum was added in a laboratory batch experiment. In a field
387 study, Shi et al. (2001) reported a 92% reduction in NH₃ loss. Moore and Edwards (2005) have
388 shown that chemical amendment improves yields due to increased N efficiency. Future work
389 must examine the impact of amendments on gaseous emissions and the risk of 'pollution
390 swapping' (the increase in one pollutant as a result of a measure introduced to reduce a different

391 pollutant) (Stevens and Quinton, 2008), which must be considered when evaluating amendments
392 for possible recommendations to legislators.

393

394 4.2. Water quality

395

396 The DRP and TP concentrations in runoff water from grass only treatment was well in excess of
397 the MAC of 30 $\mu\text{g DRP L}^{-1}$ (Flanagan, 1990) and 25-100 $\mu\text{g TP L}^{-1}$ (USEPA, 1986) for fresh
398 waterbodies.

399

400 This study validated the results of a micro-scale study (Brennan et al., 2011) at meso-scale and
401 demonstrated that PAC is the most effective chemical amendment to reduce incidental DRP
402 losses, with alum being most effective at reducing DUP, PP, TP and SS losses arising from land
403 application of dairy cattle slurry. A limited number of runoff studies have been carried out with
404 chemical amendment of dairy cattle slurry (Elliot et al, 2005; Torbert et al., 2005) and swine
405 slurry (Smith et al., 2001b). Torbert et al. (2005) amended landspread composted dairy manure
406 with ferrous sulphate, gypsum and lime (each at 3:1 metal-to-TP ratio) immediately prior to a 40-
407 min rainfall event with overland flow equivalent to a rainfall intensity of 12.4 cm h^{-1} . Ferrous
408 sulphate reduced DRP loss by 66.3%, while gypsum and lime amendments increased DRP loss.
409 Lime and gypsum were effective for a short time at the beginning of the event and the authors
410 recommended that lime could be used in areas with infrequent and low volume runoff events. In
411 the Torbert et al. (2005) study, amendments were surface applied to slurry immediately after
412 slurry application and just before the first rainfall simulation event occurred. The differences
413 between the results are likely due to a combination of the shorter contact time with lime before

414 the first rainfall event and less mixing due to different amendment application methods used in
415 each study. In a plot study, Smith et al. (2001b) amended swine manure with alum and AlCl_3 at
416 two stoichiometric ratios (0.5:1 and 1:1 Al: TP). Dissolved reactive phosphorus reductions for
417 alum and AlCl_3 at the lower ratio were 33 and 45%, respectively, with 84% for both amendments
418 at the higher ratio, which was similar to reductions observed in the current study.

419
420 The reductions in P losses in the present study were similar to the percentage reductions obtained
421 in other incidental P loss mitigation studies. Hanrahan et al. (2009) reported that incidental TP
422 and DRP losses were reduced by 89 and 65%, respectively, by delaying rainfall from 2 to 5 days
423 after dairy cattle slurry application. This was in agreement with results of O'Rourke et al. (2010).
424 In a plot study, McDowell and Sharpley (2002) applied dairy cattle slurry at $75 \text{ m}^3 \text{ ha}^{-1}$ to the
425 upper end of plots with lengths varying from 1 to 10 m. Increasing the distance from the location
426 where dairy slurry was applied to the runoff water collection point was shown to reduce
427 incidental P concentrations in overland flow by between 70 and 90% when plots were subjected
428 to simulated rainfall with an intensity of 70 mm h^{-1} . Therefore, as there are less expensive
429 methods which can achieve similar reductions in incidental P losses, in future the focus of
430 chemical amendment studies must be to find amendments to bind P in soil with the aim of
431 reducing chronic P losses.

432
433 In order to minimise the effect of the larger variation in the study control than in runoff from
434 grass-only and amended slurry runoff boxes and to detect differences between treatments, the
435 slurry-control was excluded from the statistical analysis of TP and PP. The reduction in TP and
436 PP losses when alum, PAC and FeCl_2 was added to slurry was a result of a combination of

437 precipitation and floc formation, which led to a decrease in SS loss in runoff water. In the case of
438 lime addition, the reductions were a result of the formation of Ca-P precipitates. The average
439 FWMC of TP for the slurry-control during the three rainfall simulation events was 8,390 $\mu\text{g L}^{-1}$.
440 This was similar to 7,000 $\mu\text{g L}^{-1}$ reported by Preedy et al. (2001) in a rainfall simulation study to
441 examine incidental P loss from dairy slurry.

442

443 Measures such as increasing the time between slurry application and the first rainfall event are as
444 effective as chemical amendment at reducing incidental losses of P. Chemical amendment
445 immobilises soluble P in slurry applied to soil and could therefore be included as a low capital
446 cost management tool to reduce farm P status and chronic P losses. The cost of chemical
447 amendments in comparison to other treatment methods (e.g. transporting to other farms,
448 anaerobic digestion, separation and composting) is likely to be the most significant factor in the
449 future implementation of chemical amendments. Economies of scale were not considered in this
450 study and this could considerably reduce costs. The cost of amendment, calculated after Brennan
451 et al. (2011), based on the estimated cost of chemical, chemical delivered to farm, addition of
452 chemical to slurry, increases in slurry agitation, and slurry spreading costs as a result of
453 increased volume of slurry due to the addition of the amendments to slurry, is shown in Table 2.
454 At the scale of the present study, alum and ferric chloride provide the best value in reducing on
455 TP loss from slurry. These are preliminary estimates and if the cost of using these amendments
456 as a mitigation measure is to be accurately calculated, then the optimum dosage for each
457 amendment at field-scale needs to be determined.

458

459 4.3. Metals in runoff water

460
461 Previous studies (Moore et al., 1998; Edwards et al., 1999) have reported that chemical
462 amendment of poultry litter posed no significant risk of increased metal release to runoff water.
463 The findings of the present study also validate this for chemical amendment of dairy cattle slurry.
464 Moore et al. (1998) associated an increase in Ca release from alum treatment to a displacement
465 of Ca in Ca-P bonds by Al. This is also likely to be the cause for PAC and FeCl₂ with Ca
466 displaced by Al and Fe. The increase in Ca from the lime treatment was expected as a high rate
467 of lime was applied. The FWMC of Fe (Fig. 8) decreased for all treatments except alum, which
468 increased Fe loss by 30% compared to the slurry-control; this was most likely a result of pH
469 effect of alum, which increased the Fe solubility leading to higher Fe losses. There are acute
470 (acute concentrations being short-term concentration and chronic being a long-term
471 concentration) MAC (750 µg L⁻¹) and chronic MAC (87 µg L⁻¹) for Al in runoff (USEPA, 2009).
472 The Al concentrations observed in the present study were below all MAC with the exception of
473 slurry-control during RS2 and grass-only treatment in RS2, which exceeded chronic MAC. There
474 is no MAC for Ca in water. Iron concentrations in runoff were all below the chronic MAC of
475 1,000 µg L⁻¹ (USEPA, 2009).

476
477 From previous studies, adverse effects are not expected due to alum amendment to manure. In a
478 plot study, Moore et al. (1998) amended poultry litter with alum to examine the effect of alum
479 amendment on runoff concentrations of metals. Alum treatment significantly reduced Fe in
480 runoff. Runoff Al concentrations were not affected by treatment and Ca concentrations increased
481 after treatment. Moore et al. (2000) also found Al loss from a small-scale catchment was
482 unaffected by alum treatment. In order to determine the effect of long-term additions of alum to

483 poultry litter, Moore and Edwards (2005) began a 20-yr study in 1995. The most significant
484 findings of this study were that long-term land application of alum-amended poultry litter did not
485 acidify soil in the same way as $\text{NH}_4\text{-N}$ fertilisers and that Al availability was lower from plots
486 receiving alum-treated poultry manure than $\text{NH}_4\text{-N}$ fertiliser. McFarland et al. (2003)
487 incorporated alum into soil prior to application of dairy dirty water and reported no difference in
488 Al concentrations in runoff between control and alum amended plots.

489

490 **5. Conclusion**

491

492 The results of this study demonstrate that chemical amendment was very successful in reducing
493 incidental losses of DRP, TP, PP, TDP, DUP and SS from land-applied slurry. The results of the
494 study demonstrate that PAC was the most effective amendment for decreasing DRP losses in
495 runoff following slurry application, while alum was the most effective for TP and PP reduction.
496 Incidental loss of metals (Al, Ca and Fe) from chemically amended dairy cattle slurry was below
497 the MAC for receiving waters. Future research must examine the long-term effect of
498 amendments on P loss to runoff, gaseous emissions, plant availability of P and metal build-up in
499 the soil. If amendments to slurry are to be recommended and adopted as a method to prevent P
500 losses in runoff, the impact of such applications on slurry-borne pathogens, as well as pathogen
501 translocation to the soil and release in surface runoff, needs to be addressed. The long-term
502 effects on microbial communities in soil must also be examined. The results of this study show
503 that even with chemical amendment, P concentration in runoff was above the MAC. Therefore,
504 amendments may not be the best option for minimising incidental P losses, as timing of
505 applications may be just as effective at controlling incidental P losses, and may be much more

506 cost effective. However, chemical amendment immobilises soluble P in slurry and has the
507 potential to reduce chronic P losses. The use of chemical amendments in combination with other
508 mitigation methods such as grass buffer strips would likely increase the effectiveness of the
509 measures. Future work should focus on using amendments to reduce P solubility in slurry to
510 decrease P loss from high P soils by binding P in slurry once it is incorporated into the soil,
511 thereby allowing farmers to apply slurry to soil without further increasing the potential for P loss.

512

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514

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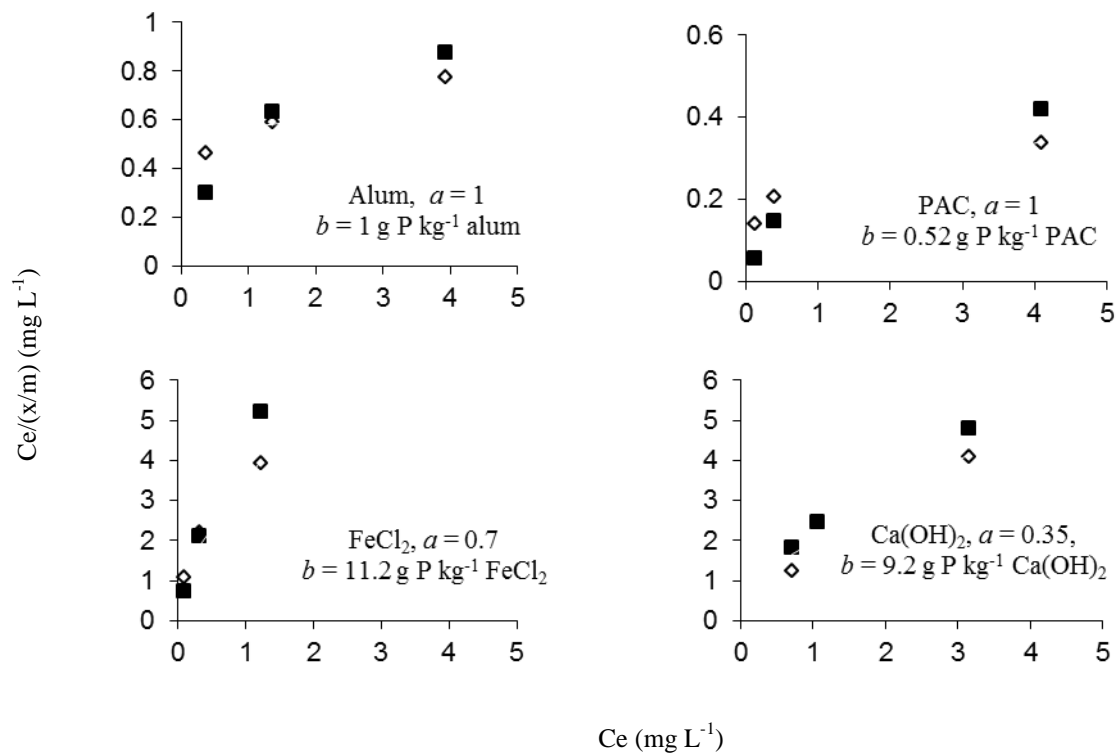
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755 Fig. 1 Langmuir isotherm fitted to phosphorus in amended slurry data

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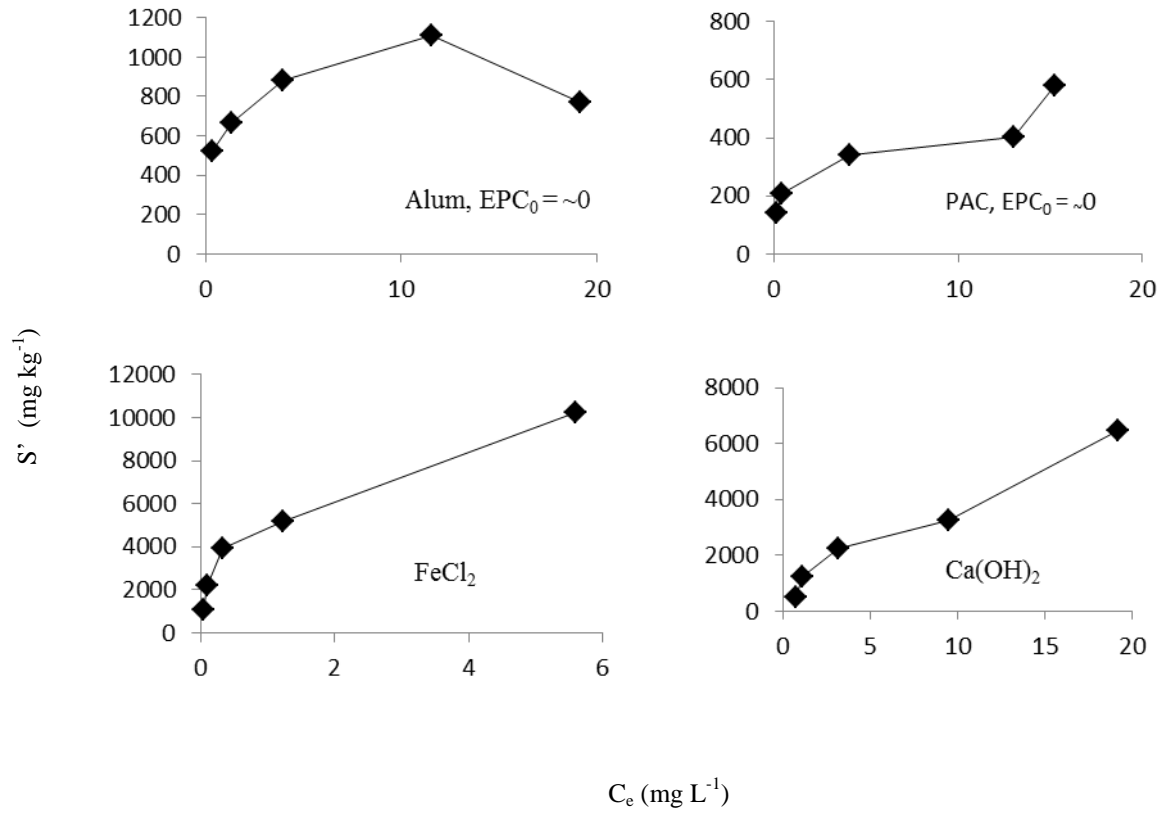
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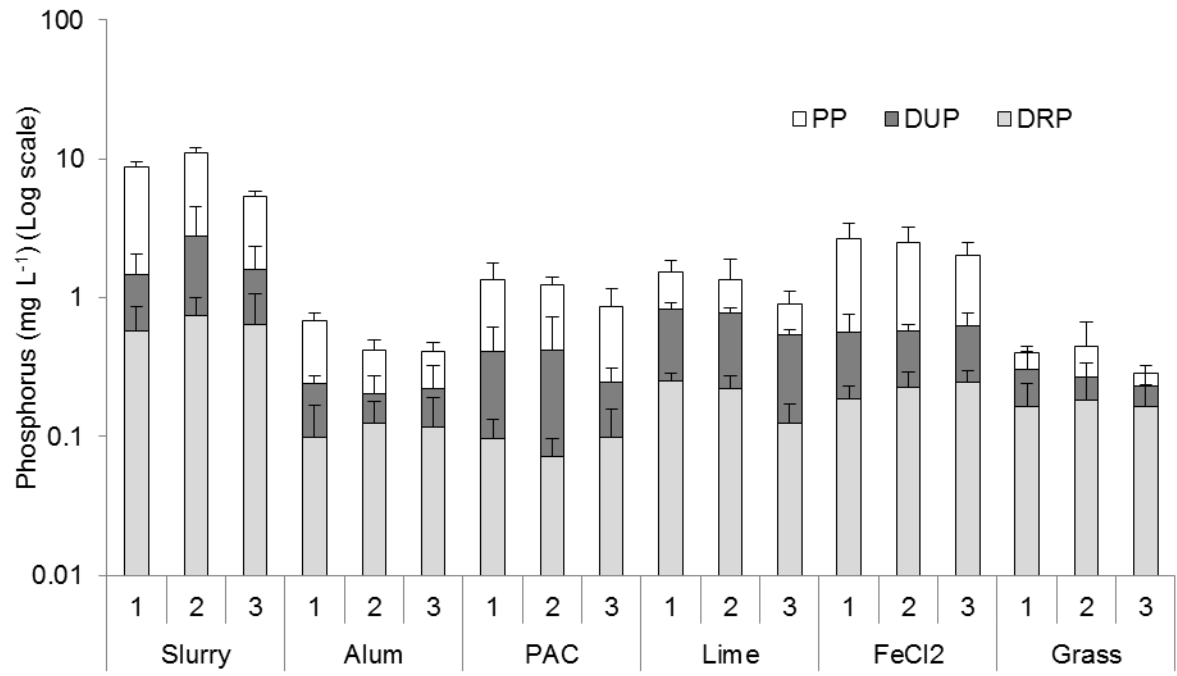
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 783 phosphorus (DUP) and particulate phosphorus (PP), which comprise total phosphorus (TP) in runoff from three
 784 rainfall simulation events.

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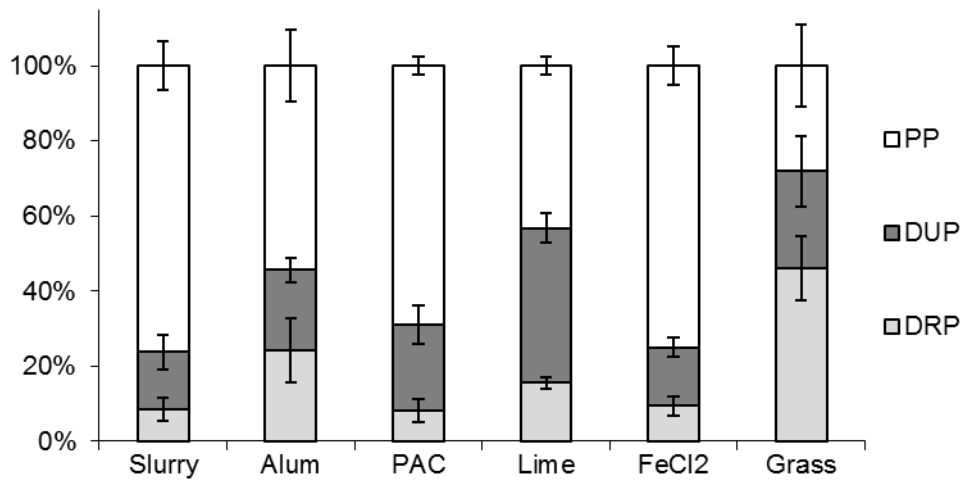
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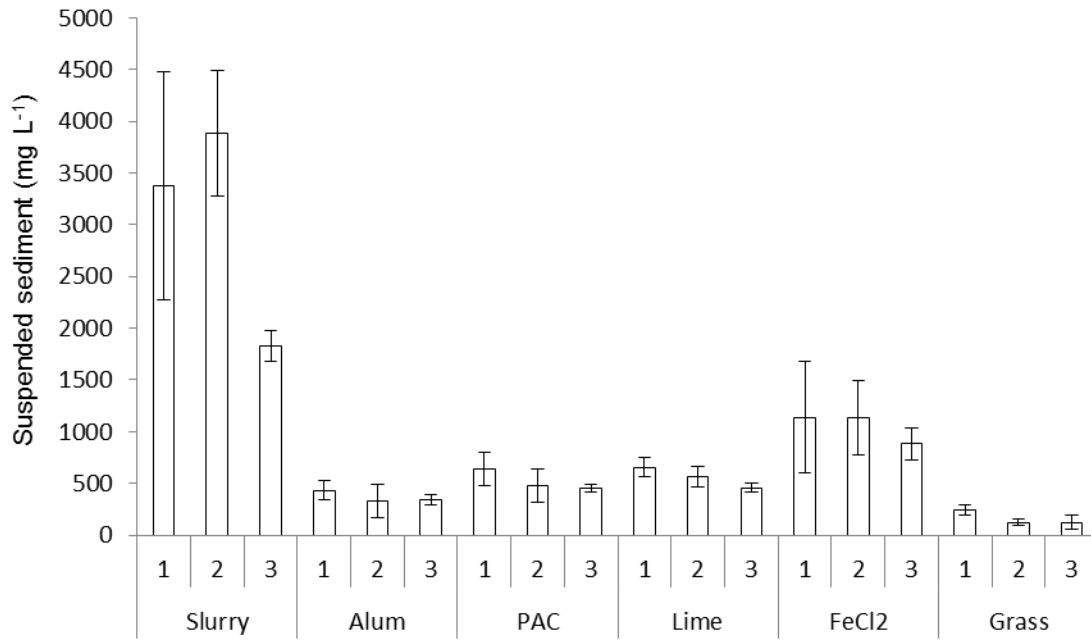
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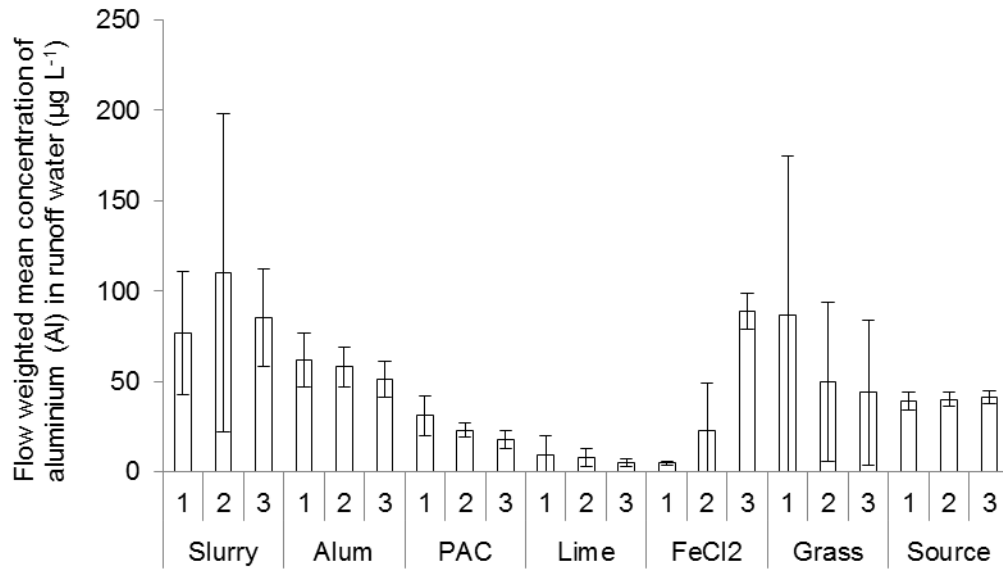
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 798 Fig 4 The average % of dissolved reactive phosphorus (DRP), dissolved un reactive phosphorus (DUP) and
 799 particulate phosphorus (PP), which comprise total phosphorus (TP) in runoff after three rainfall simulation events.
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815 Fig 5 Average flow weighted mean concentrations of suspended sediment in runoff.
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 831 Fig 6 Average flow weighted mean concentrations of Al in runoff and rain water.
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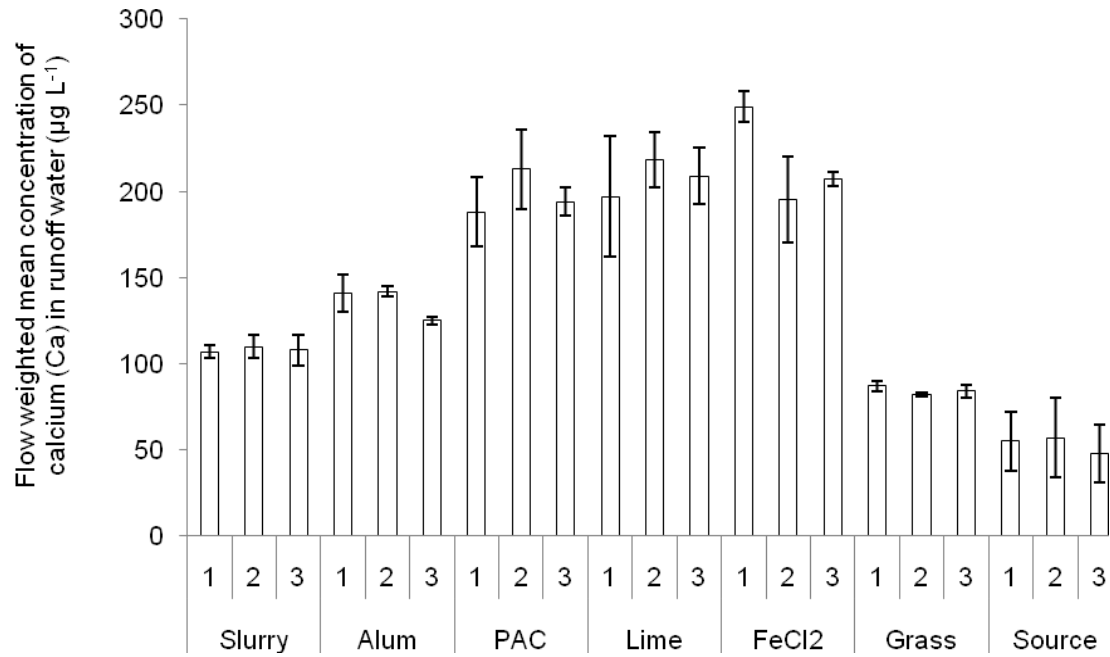
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 847 Fig 7 Average flow weighted mean concentrations of Ca in runoff and rain water.
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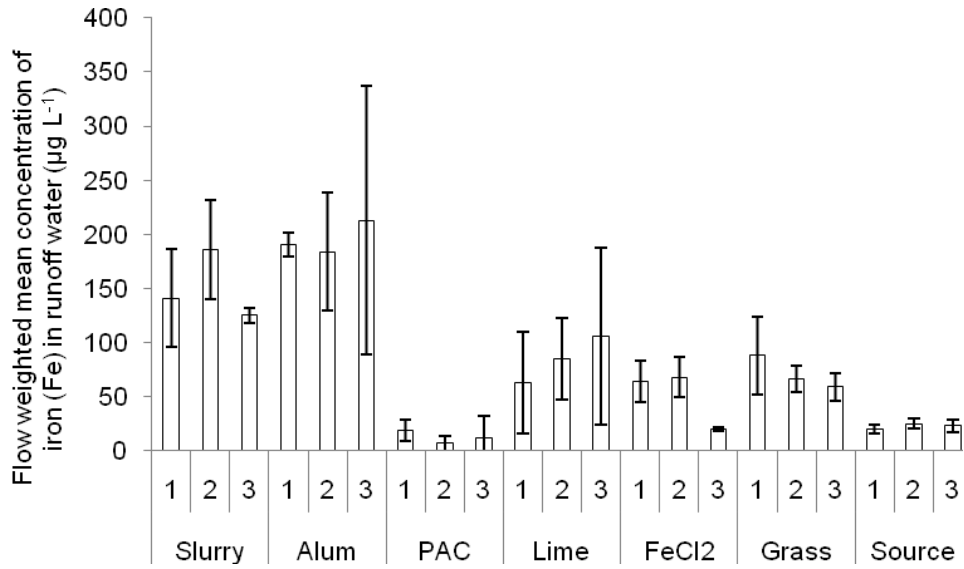


Fig 8 Average flow weighted mean concentrations of Fe in runoff and rain water.

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878 Table 1
 879 Stoichiometric ratio at which the amendments were applied and slurry dry matter (DM), pH and average
 880 concentrations of NH₄- N, water extractable phosphorus (WEP), total nitrogen (TN), total phosphorus (TP) and total
 881 potassium (TK) (n=3).

	Rate	DM %	pH	NH ₄ -N mg L ⁻¹	WEP g kg ⁻¹ DM	TN mg L ⁻¹	TP mg L ⁻¹	TK mg L ⁻¹
Slurry		10.5 (0.04)	7.47 (0.05)	1760 (123)	2.22 (0.34)	4430 (271)	1140 (76)	4480 (218)
Alum	1.1:1 [Al:TP]	9.4 (0.16)	5.40 (0.12)	1770 (21)	0.002 (0.0004)	4570 (176)	1140 (69)	4360 (84)
PAC	0.93 [Al:TP]	9.6 (0.28)	6.37 (0.05)	1760 (143)	0.0013 (0.0003)	4750 (448)	1180 (165)	4680 (448)
Lime	10:1 [Ca:TP]	8.2 (0.29)	12.2 (0.12)	1320 (141)	0.0056 (0.0003)	3190 (263)	1140 (96)	4810 (227)
FeCl ₂	2:1 [Fe:TP]	10.1 (0.22)	6.7 (0.06)	1700 (11)	0.0022 (0.0006)	4340 (372)	1120 (51)	4720 (386)

882 () standard deviation

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888 Table 2
 889 From preliminary study and current study, showing cost of treatments and total phosphorus (TP) lost from runoff box.

Treatment	Preliminary agitator test ^a		Runoff box		Cost per m ³ treated slurry ^b	TP loss as % of TP applied	Cost per kg P reduction	P lost per hectare
	stoichiometric ratio	DRP reduction	stoichiometric ratio	DRP reduction				
	metal: TP	%	metal: TP	%	€m ⁻³		€kg P ⁻¹	kg P ha ⁻¹
Slurry	-	-	-	-	1.90	7.70	-	2.90
Alum	0.98:1	87	1.11:1	83	7.40	0.46	66.70	0.17
PAC (AlCl ₃) ^c	0.98:1	88	0.93:1	86	8.80	1.05	91.10	0.40
Lime	5:1	74	10:1	69	10.20	1.16	111.00	0.44
FeCl ₂	2:1	88	2:1	67	7.00	2.20	61.00	0.19

890 ^aTaken from Brennan et al. (2011).

891 ^b The cost m⁻³ and cost effectiveness have been updated from Brennan et al. (2011) to reflect the slight change in ratio of metal:TP in the present runoff box study.

892 ^cLaboratory grade aluminium chloride (Al₂(SO₄)₃.nH₂O) was used in Brennan et al. (2011). Commercially available commercial grade liquid poly-aluminium chloride was used in the present study.

893 Note: All treatments were found to be significantly different to the control (p<0.001) in the Brennan et al. (2011) study. However, these were not significantly different to each other. In this study, all
 894 treatments were significantly different to the slurry-control. Alum and AlCl₂ were significantly different to lime and FeCl₂, but not to each other. (€1.00 is approximately equal to \$1.37 or £1.59)

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