Effect of chemical amendments to dairy soiled water and time between application and rainfall on phosphorus and sediment losses in runoff

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Abstract

Dairy soiled water (DSW) is a dilute, low nutrient effluent produced on Irish dairy farms through the regular washing down of milking parlours and holding areas. In

26 Ireland, there is no closed period for the land application of DSW except where heavy

27 rain is forecast within 48 h. Chemical amendments have the potential to decrease

28 phosphorus (P) and suspended sediment (SS) loss from DSW applied to land. This

29 study examined the impact of three time intervals (12, 24 and 48 h) between DSW

30 application and rainfall and five treatments (control, unamended DSW, and DSW

31 amended with lime, alum or ferric chloride ($FeCl_2$)) on P and sediment losses from an

32   intact grassland soil in runoff boxes. Rainfall was simulated at 10.5 ± 1 mm h^{-1}.

33 Phosphorus concentrations (1-1.6 mg L^{-1}) in runoff from DSW application, while not

34   quantitative measures of P loss to surface waters in the field, indicated the importance

35   of incidental P losses and that the current 48 h restriction in Ireland is prudent.

36 Unamended DSW application increased P loss by, on average, 71 %, largely due to an

37 increase in particulate phosphorus (PP) loss. All three amendments were effective in

38 decreasing P and SS losses in runoff and, apart from the SS results for lime, were

39   significantly different ($p<0.05$) to the control at at least one time point. Lime (a 64 %

40 reduction in total phosphorus (TP) in comparison with DSW only) was less effective

41 than alum or $FeCl_2$, likely due to the lower solubility of $CaCO_3$ in water. Chemical

42 amendment showed potential to decrease P losses from land application of DSW, but

43 the efficacy of such amendments would need to be assessed in field trials and a cost-

44 benefit analysis conducted to further examine whether they could be practically

45 implemented on farms.

46

47 *Keywords*: Dairy soiled water; farm effluent; application timing; incidental loss;

48 chemical amendment.

49

50   **1. Introduction**

3

51

52 Livestock production based on grazed grassland is associated with inputs of nitrogen

53 (N) and phosphorus (P) to soils, including dung and urine deposition, chemical

54   fertilizers, and organic fertilizers (manures and slurries). Dairy soiled water (DSW) is

55 one such organic fertilizer on dairy farms. It consists of wash-water from the milking

56 parlour and holding areas for livestock, which contains parlour washings, livestock

57 faeces and urine. In Ireland, DSW is defined as a wastewater with a 5-d biochemical

58 oxygen demand (BOD5) of less than 2,500 mg L^{-1} and a dry matter (DM) content of

59   less than 1 % (SI 610 of 2010), distinguishing it from more concentrated cattle

60 slurries. Dairy soiled water is generated every d on dairy farms and can be highly

61 variable in composition. Martínez-Suller et al. (2010) found that, due to management

62 practices, BOD5 can reach as high as 8,400 mg L^{-1} and DM can be far in excess of 1

63 %. However, in a survey of 60 Irish dairy farms over a year, Minogue et al. (2010)

64 found that mean BOD5 concentration was 2,246 mg L^{-1} and mean DM was 0.5 %, and

65 most samples were below the BOD5 and DM limits. Application to land is the most

66 common method for disposal of DSW, as it has a high nitrogen fertilizer replacement

67   value (Minogue et al., 2011). However, there is a risk of nutrient (N and P) loss

68   associated with land application of all types of slurries and DSW (Di et al., 1998;

69   Woodard et al., 2002; Withers and Bailey, 2003; Ryan et al., 2006), particularly

70   incidental P losses in runoff, when rainfall events follow shortly after P application to

71   the soil. Such incidental losses can account for a large portion of P loss from

72   agricultural fields (Sharpley and Tunney, 2000).

73

74 The Statutory Instrument (SI) governing the application of DSW to land in Ireland (SI

75   610 of 2010) limits application at 50 m^3 ha^{-1} over any 42-d period and specifies that it

4

76 cannot be applied to land if heavy rain is forecast within 48 h of application. Unlike

77 more concentrated cattle slurries, DSW is not subject to a 'closed period' for

78 application in the winter months when soils tend to be wet and heavy rainfalls

79 associated with Atlantic depressions occur. It can be very difficult to forecast rain

80 events in Ireland, particularly in winter months, and application is likely to occur at

81 time intervals shorter than 48 h before heavy rain in some instances. No study has, to

82 date, examined the impact of short time durations between DSW application and

83 surface runoff of nutrients and suspended sediment (SS). Potential methods to

84 mitigate nutrient and SS loss in runoff when rainfall occurs at these time intervals also

85 warrant investigation.

86

87 The potential of chemical amendments, such as lime, gypsum, alum and ferric

88 chloride, to decrease P loss from soils has been investigated by numerous researchers

89 (e.g. Callahan et al., 2002; Zvomuya et al., 2006; Murphy and Stevens, 2010). There

90 has also been some investigation of the impacts of amendments to agricultural

91 wastewaters, in particular, manure (Kalbasi and Karthikeyan, 2004; Brennan et al.,

92 2011) or poultry litter (Moore and Edwards, 2005), on surface runoff of nutrients,

93 metals and SS. These and other studies reported that there was no increased risk of

94 heavy metal release to runoff water, following chemical amendment of poultry litter

95 or agricultural wastewaters (Moore et al., 1998; Edwards et al., 1999; Brennan et al.,

96 2011). However, little work has been conducted on DSW (Fenton et al., 2011). The

97 mode of addition of chemicals to wastewater may vary between incorporation into

98 soil (Novak and Watts, 2005; Murphy, 2007), direct addition to manure (Moore et al.,

99 1998), or addition after application of manure to land (Torbert et al., 2005). Brennan

100 et al. (2011) found that poly-aluminum chloride hydroxide (PAC), added at 0.93:1

101 aluminum (Al):total phosphorus (TP) of slurry, reduced dissolved reactive phosphorus

102 (DRP) by up to 86 %, compared with the surface runoff from dairy cattle slurry alone;

103 while alum, added at 1.11:1 Al:TP of slurry, was most effective in reducing SS (88

104 %), TP (94 %), particulate phosphorus (PP) (95 %), total dissolved phosphorus (TDP)

105 (81 %), and dissolved un-reactive phosphorus (DUP) (86 %). Fenton et al. (2011)

106 investigated the use of chemical amendments to reduce P losses arising from the land

107 application of DSW to grassland in a desk-scale experiment and found that the most

108 effective chemicals were alum (72 % reduction), $FeCl_2$ (89 % reduction) and lime (83

109 % reduction). Therefore, these three amendments were selected for further study in

110 the present laboratory runoff experiment.

111

112   The aim of the present study was to examine the effect of (1) high intensity rainfall

113 events after 12, 24 and 48 h of land application of DSW to grassland, and (2)

114 chemical amendment of DSW on losses of P and SS in runoff.

115

116   **2. Materials and Methods**

117

118 Intact 0.1 m-deep and 0.5 m-long soil cores were collected from grassland, which had

119 not received fertiliser applications for more than 10 y, in Galway City, Republic of

120   Ireland (53°16'N, 9°02' W). Soil cores (n=3) taken to a depth of 0.1 m below the

121 ground surface from the same location, were air dried at 40 °C for 72 h, crushed to

122 pass a 0.002 m sieve, and analysed for Morgan's P (Pm; the national test used for the

123   determination of plant available P in Ireland) using Morgan's extracting solution

124 (Morgan, 1941). Water extractable phosphorus (WEP) was measured by shaking 0.5 g

125   of soil in 40 ml of distilled water for 1 h, filtering (0.45 µm) the supernatant water and

126   determining P colorimetrically. The soil cores were kept separate for analysis and

127 replication (n=3) was used in analysis of each of the 3 cores. Soil pH (n=3 from each

128 of the soil cores) was determined using a pH probe and a 2:1 ratio of deionised water-

129   to-soil. Particle size distribution (PSD) was determined using B.S.1377-2:1990 (BSI,

130   1 990a) and the organic matter content of the soil was determined using loss on

131   ignition (B.S.1377-3; BSI, 1990b).

132

133 **2.1 Dairy soiled water sampling and analysis**

134

135 Dairy soiled water produced from the concrete holding areas (non-scraped) and

136 milking parlour washings of 137 spring calving dairy cows (milked twice daily) at the

137 Environmental Research Centre (Teagasc, Wexford), was collected in March, 2011.

138 High pressure hoses were used to clean the yards. There were three tanks, connected

139 in series, with a total capacity of approximately 52 m^3 and a working capacity of

140 approximately 80 %. The tanks were agitated for 20 min until the DSW was

141 homogenized, and DSW was collected in a 10-L plastic drum and transported to the

142   laboratory in a temperature-controlled container within one d of sample collection.

143 The DSW was stored at 4 °C until immediately prior to the start of the experiment

144 (about 2 d after sample collection). The sample was fully analysed colorimetrically for

145 the following water quality parameters using a nutrient analyser (Konelab 20, Thermo

146   Clinical Labsystems, Finland) (each tested at n=3 and, with the exception of TP,

147 filtered through a 0.45 µm filter): ammonium-N (NH_4-N), nitrite-N (NO_2-N), nitrate-

148 N (NO_3-N), total ammoniacal N (TAN), DRP and TP (after acid persulphate

149 digestion) in accordance with the standard methods (APHA, 2005). To test for TAN,

150 50 ml of DSW was diluted in 1 L 0.1M HCl and then tested in the nutrient analyser.

151 pH was measured using a pH probe (WTW SenTix 41 probe with a pH 330 meter,

152 WTW, Germany) and the DM content was determined by drying at 40°C for 72 h.

153

154 **2.2 Experimental treatments**

155

156   The five treatments examined in this study were: (1) control (grassed soil only), (2)

157 unamended DSW, and DSW amended with either (3) aluminium sulphate 18-hydrate

158   ($Al_2(SO_4)_3 \cdot 18H_2O$) (alum), (4) analytical grade $FeCl_2$, or (5) burnt lime ($Ca(OH)_2$).

159 Amendments were applied at stoichiometric ratios determined from Fenton et al.

160   (2011). Alum was applied at a rate of 8.8:1 (Al:TP), ferric chloride at a rate of 200:1

161 (Fe:TP), and lime at a rate of 2,500:1 (Ca:TP). Amendments were added to the DSW

162 and mixed rapidly (10 min at 100 rpm) using a jar test flocculator immediately prior

163 to application to runoff boxes. The temperature of the laboratory in which the

164 experiments were conducted was approximately 10 °C. Two replicates of each

165 treatment were subject to rainfall at a time interval between treatment application and

166   rainfall of either 12, 24 or 48 h, giving a total of 30 runoff boxes (5 treatments x 3

167   time intervals x 2 replicates). The limited replication involved (n=2) was due to

168   limited availability of soil samples from the study site and, in order to take this into

169 account, the formal inference was conducted in an exploratory manner rather than as

170 evidence of cause and effect as would be normal for a designed experiment.

171   Relationships identified were taken as indicating association only.

172

173 **2.3 Runoff boxes and rainfall simulation set-up**

174

175 This experiment used two laboratory runoff boxes, 1-m-long by 0.225-m-wide by

176 0.05-m-deep with side walls 0.025 m higher than the soil surface and 0.005-m-

177   diameter drainage holes each located at 0.3-m-intervals along the base (after Regan et

178   al., 2010). The runoff boxes were positioned at an angle of 5 degrees to the horizontal

179 and all surface runoff was collected with an overflow weir, positioned at the same

180   level as the soil surface, and a funnel. Cheese cloth was placed at the base of each

181 runoff box before placing the soil cores. Intact grassed cores from the study site were

182   transported to the laboratory and stored at 11°C in a cold room prior to testing. All

183   experiments were carried out within 14 d of soil core collection. Immediately prior to

184 the start of each runoff box experiment, the cores were trimmed and placed in the

185 runoff box. Each core was butted against its adjacent core to form a continuous

186 surface. Molten candle wax was used to seal any gaps between the cores and the sides

187 of the runoff box.

188

189 The packed cores were then saturated until ponding occurred on the soil surface using

190   a rotating disc, variable-intensity rainfall simulator (after Williams et al., 1997), and

191 left to drain for 24 h before the experiment commenced. All soils were approximately

192 at field capacity prior to the start of each experiment. Dairy soiled water and amended

193 DSW were applied to the surface of the intact grassland soil in runoff boxes at a rate

194 equivalent to 50 m^3 ha^{-1}, the legal limit for application in any 42-d period. The DSW

195 and chemically-amended DSW were spread evenly across the soil surface.

196

197 The rainfall simulator consisted of a single 1/4HH-SS14SQW nozzle (Spraying

198 Systems Co., Wheaton, IL) attached to a 4.5-m-high metal frame, and calibrated to

199 achieve an intensity of 10.5±1 mm h^{-1} (rainfall with a return period of about 3 y in

200 Ireland; Met Eireann, 2012) and a droplet impact energy of 260 kJ mm^{-1} ha^{-1} at 85 %

201 uniformity. During each rainfall simulation, the drainage holes were sealed to

202   replicate conditions of saturation excess runoff. Significant surface runoff (determined

203 once consistent, continuous droplets of water flowed from the flume) typically began

204   within 20-30 min. Runoff was collected for this initial period and then 5, 10, 15, 20,

205 25, 30, 40, 50 and 60 min thereafter. The volume of water collected during each time

206 interval was measured and collection of runoff ceased at the 60-min sampling interval.

207 The water used in the rainfall simulations was tap water, which had a DRP

208   concentration of less than 0.005 mg L^{-1}, a pH of 7.7±0.2 and an electrical conductivity

209 (EC) (measured using a LF 96 Conductivity Meter, WTW, Germany) of 0.435 dS m^{-1}.

210 The calcium (Ca^{2+}) concentration of the tap water, measured by atomic absorption

211 spectrophotometry (AAS), was 3.11 mg L^{-1} and was higher than the annual mean

212 concentration of Ca$_{2+}$ in rainwater (0.85 mg L^{-1}) measured between 1992 and 1994 for

213 Ireland (Jordan, 1997). This may have impacted somewhat on measurements, but

214 owing to availability, the same source has been used in similar experiments (Regan et

215 al., 2010). Water pH was measured immediately prior to each event using a pH and

216   electrical conductivity meter.

217

218 **2.4 Runoff analysis**

219

220 Immediately after collection, runoff water samples were passed through a 0.45 µm

221 filter and a subsample was analysed colorimetrically for DRP. A second filtered

222 sample was analysed for TDP using acid persulphate digestion (APHA, 2005),

223 followed by spectrophotometry using a nutrient analyser (Konelab 20, Thermo

224 Clinical Labsystems, Finland) after Murphy and Riley (1962). Unfiltered runoff water

10

225 samples were also collected and TP was measured using acid persulphate digestion,

226 followed by spectrophotometry. Total P comprised PP and TDP, with TDP consisting

227 of DRP and DUP. Particulate phosphorus was calculated by subtracting TDP from

228 TP. Suspended solids were determined for all samples by vacuum filtration of well-

229 mixed runoff water through Whatman GF/C (pore size: 1.2 µm) filter paper. All

230 samples were tested in accordance with the Standard Methods (APHA, 2005). All

231 reported concentrations in this paper were flow-weighted mean concentrations

232 (FWMC) calculated based on surface runoff volume, collected in each time interval,

233 and the measured concentrations.

234

235   **2.5 Statistical Analysis**

236

237 The analysis was conducted as an ANOVA of the factorial combinations of treatment

238 and time. There were five levels of treatment (control, unamended DSW, lime, $FeCl_2$

239 and alum) and three levels of the time factor (12, 24 and 48 h). Due to the limited

240   replication, it was not feasible to account for all structural effects in the experiment.

241 Large differences in variance between treatments were taken into account in a

242 heterogeneous variance mixed model using the Mixed procedure of SAS (2009). The

243 repeated measures aspect of the experiment was not modelled. Tukey adjustments

244 were made to account for multiplicity in comparison of means. Pearson product-

245 moment correlations were used to examine association between PP and SS. The

246 relationship between SS and volume was examined using analysis of covariance,

247 regressing SS and other relevant variables on volume. Residual checks showed no

248 evidence that the distributional assumptions of the analysis were not met.

249

250   **3. Results and Discussion**

251

252 **3.1 Soil and dairy soiled water characterisation**

253

254 The characteristics of the soil and DSW used in this study are tabulated in Tables 1

255   and 2, respectively. The grassland sandy loam soil used in this study was a well-

256 drained sandy loam Acid Brown Earth (WRB classification: Cambisol). The soil pH,

257   at 6.4, was optimal for grass growth and P plant-availability. It had a relatively low

258 Morgan's P concentration of 2.8 mg L^{-1}. This soil would be classified as an Index 1

259   soil in the Irish grassland soil P index system (SI 610 of 2010) and would therefore

260 not be perceived as being a high risk for P loss to water in terms of its P content.

261 Agronomic advice to increase grass production would be to apply additional P to this

262   soil in order to build up soil reserves of P. This soil could receive P at rates up to a

263 maximum of 49 kg available-P ha^{-1} y^{-1}. In this study, based on the P content of the

264 DSW (Table 1) and an application rate of 50 m^3 ha^{-1}, the soil was loaded at 0.7 kg P

265   ha^{-1} y^{-1}.

266

267 Dairy soiled water used in the study had a DM content of 0.2 % (Table 2). This would

268 place it within the legally defined threshold for soiled water of 1 % DM and at the

269 more dilute end of the range of DSW concentrations found on Irish farms (average of

270 0.5 %; Minogue et al., 2010). In terms of P content (14.2 mg TP L^{-1}), this DSW was

271   also relatively dilute (average of 80 mg L^{-1}; Minogue et al., 2010). The proportion of

272 TP as DRP, at 51 %, was typical of DSW composition on Irish dairy farms. The bulk

273 of the remaining TP was likely in organic form. The N content (730 mg total nitrogen

274 (TN) L^{-1}) of this DSW was fairly typical (average of 587 ± 536 mg L^{-1}; Minogue et

275 al., 2010), but the proportion of TN as NH_4-N was relatively low (15 %, compared to

276   36 %).

277

278 **3.2 Phosphorus loss in runoff**

279

280 The FWMC of P speciation for the control (grass only), DSW only, and amended

281 DSW treatments for all three rainfall events are presented in Figure 1 a. The

282 interaction of time and treatment was significant for DRP, TP, PP and SS ($P < 0.001$).

283 Generally, the highest concentrations of P in runoff occurred during the first 20 min of

284 the commencement of runoff, before reaching steady state. Mean TP concentrations in

285 surface runoff from the control ranged from 202 µg L^{-1} (0.03 kg ha^{-1}) to 486 µg L^{-1}

286   (0.09 kg ha^{-1}) (Figure 1). Most of this P was present in dissolved un-reactive form (44

287 %) or particulate form (36 %), whereas only 20 % was in dissolved reactive form. The

288 results indicated that P concentrations in surface runoff water from a low P index soil

289 such as this may exceed the maximum allowable concentration (MAC) for discharge

290 to receiving waters of 0.03 mg L^{-1} (2000/60/EC: Council of the European Union,

291   2000), despite its low P content.

292

293 It must be borne in mind that this experiment only assessed P loss in runoff from an

294   isolated 0.225 m^2 area of soil with a relatively steep slope, relatively intense and

295   persistent rainfall, and with no capacity to drain water vertically (saturation excess

296   runoff). In the field, rainfall would typically be less intense and persistent, and the soil

297 would typically have the capacity for vertical drainage. Therefore, the experiment

298   replicated a worst-case scenario in terms of potential incidental P loss from soil. In

299   small-scale experiments, the attenuation of contaminants during transport is limited.

300 Therefore, while P losses from the runoff boxes may be used to judge the relative

301 merit of chemical amendments and the effects of time interval, they are not

302 quantitative measures of P loss to surface water bodies that might be expected in the

303 landscape.

304

305 Application of un-amended DSW increased concentrations of TP in runoff

306 significantly (Figure 1) to 1.6 mg L^{-1} (total loss of 0.3 kg ha^{-1}) for the 12-h rainfall

307 event ($p<0.0001$), 0.96 (total loss of 0.18 kg ha^{-1}) for the 24-h event ($p<0.008$) and

308 0.94 mg L^{-1} (total loss of 0.16 kg ha^{-1}) for the 48-h event ($p<0.0017$). This highlights

309 the potential importance of incidental P losses when heavy rain follows soon after

310 application of a P source to soil, with TP losses being over three times greater than the

311 control at 12 h.

312

313 Total P concentrations in runoff from both the control and unamended DSW

314 treatments tended to decrease with time interval between treatment application and

315 rainfall (Figure 1). This decrease in concentration was coincident with a decrease in

316 runoff volume (e.g. from 4,057 to 3,414 to 3,266 ml for the 12, 24 and 48 h time

317 intervals, respectively, for the control treatment). It would appear that, due to a longer

318 time draining before rainfall was initiated (36, 48 and 60 h after saturation for the 12,

319 24 and 48 h time intervals, respectively), antecedent soil moisture conditions were

320 different, giving the longer time interval soils a greater capacity to infiltrate and store

321 rainfall. The higher soil water content and lower infiltration and storage capacity of

322 the 12 h time interval soils may have forced more of the water to flow directly over

323 the soil surface, mobilising P that is typically concentrated in the upper surface of

324 grassland soils. The soil used in the runoff boxes came from the top 5 cm of the soil

325 profile and will have a higher concentration than the top 10 cm of soil as shown in

326 Table 1. This mechanism would be consistent with greater concentrations of PP in

327 runoff from the 12 h treatment (Figure 1) as PP loss is associated with water flow over

328 the soil surface and it is the uppermost surface soil that influences the concentration of

329 P in surface runoff most (Sharpley, 1980).

330

331 As the proportional decrease in P concentrations with time interval was similar for

332 both the control and the unamended DSW treatments, due to antecedent soil moisture

333 conditions, it seems unlikely that there was any effect of time interval between DSW

334   application and rainfall on P loss. This suggests that the measures in SI 610 of 2010

335 restricting DSW application when heavy rain is forecast within 48 h are prudent to

336   decrease the potential for pollution of receiving waters. It is, of course, likely that as

337 the time interval between application and heavy rain widens further, P losses are

338   likely to decrease due to further interaction with the soil and plant uptake.

339

340 As with the control, DRP concentrations in runoff from the unamended DSW

341 treatment were relatively low (Figure 1). Despite DRP making up 51 % of TP in the

342 DSW, most of the increase in TP concentrations relative to the control was due to

343 increased PP and DUP loss (Figure 1). Particulate P constituted 75 % of the total mass

344 of P released over the three rainfall events. Usually the predominance of dissolved

345   forms of P in runoff reflects particle retention by the vegetation and limited erosion

346   due to vegetative cover and the absence of livestock (Haygarth et al., 1998; Hart et al.,

347 2004). It is likely that DRP in DSW was sorbed rapidly by the soil (Maguire et al.,

348 2001), while PP may have been more susceptible to mobilisation and loss at the soil

349 surface (Regan et al., 2010). Given that the PP content of DSW is typically quite low

350 (Minogue et al., 2010), it would seem likely that DRP added in the DSW may have

351 sorbed to soil particles which were then lost in runoff.

352

353 Dissolved un-reactive phosphorus concentrations in runoff from the unamended DSW

354 treatment were also higher than the control. This probably reflects mobilisation of

355 DUP added in the DSW (Brennan et al., 2011). The DUP fraction is generally

356 considered to consist largely of dissolved organic P (Toor et al., 2003; Murphy et al.,

357 2010). This organic P is generally not as bioavailable as reactive forms, but can

358 become bio-available and contribute to eutrophication in receiving water bodies

359 through chemical or enzymatic hydrolisation (Correll, 1998)

360

361 All three amendments to DSW were effective in decreasing P concentrations in runoff

362 relative to the unamended DSW treatment (Figure 1). Lime decreased the FWMC of

363 TP (average across the three rainfall events) by 66 % (p<0.07), whereas alum and

364 FeCl2 were more effective, decreasing concentrations by 84 (p<0.005) and 83 %

365 (p<0.007), respectively. For all three amendments, most of the decrease in TP loss

366 was due to a decrease in PP and DUP loss relative to the unamended DSW treatment.

367 This is most likely due to the fact that all three amendments release effective

368 flocculants (Ca^{2+}, Fe^{2+} and Al^{3+}) into the DSW solution, leading to flocculation and

369 removal of PP and DUP from suspension (Brennan et al., 2011). These flocculants

370 may also aid adhesion of particles in the DSW to soil particles and adhesion of soil

371 particles themselves, further decreasing P losses in runoff (Brennan et al., 2011).

372

373 Lime was less effective than the other two amendments, largely due to high losses of

374 DUP relative to both the unamended DSW treatment and the control. The lime

16

375 amendment increased the pH of surface runoff, giving an average pH of 8.9±0.13

376 across the three rainfall events, while the other amendments produced surface runoff

377 with a pH similar to that of the unamended DSW treatment (6.9±0.14). Liming is

378 often associated with an initial flush of soluble organic matter and dissolved organic P

379 release that can increase P losses in runoff or leachate, at least temporarily (Murphy,

380 2007). At the higher pH of the limed DSW treatment, organic P can be more soluble

381 due to desorption or dispersion of organic matter, or release of organic P through

382 increased microbial activity (Hannapel et al., 1964). Dissolved un-reactive

383 phosphorus made up a greater proportion of TP for the lime amendment than the other

384 two chemically amended DSW treatments. Most of the DUP in runoff is likely to be

385 dissolved organic P. Lime also increased DRP losses relative to the control and

386 unamended DSW treatment for the 24-h rainfall event. Such inconsistent effects of

387 lime on DRP solubility have been found by others (Murphy and Stevens, 2010).

388

389 Alum and $FeCl_2$ were also more effective than lime in decreasing PP loss ($p<0.05$)

390 despite the fact that the Ca:TP stoichiometric ratio in the lime-amended DSW

391 (2,500:1) was much greater than the Al:TP ratio in the alum treatment (8.8:1) and the

392 Fe:TP ratio in the $FeCl_2$ treatment (200:1). This is likely due to the lower solubility of

393 $CaCO_3$ in water (15 mg L^{-1}) than aluminium sulfate (364,000 mg L^{-1}) and iron

394 chloride (920,000 mg L^{-1}), delivering concentrations of flocculant four orders of

395 magnitude less. In a desk-scale experiment examining the feasibility of alum, $FeCl_2$

396 and lime to decrease P loss from land application of DSW, Fenton et al. (2011) found

397 that alum was the most feasible, followed by $FeCl_2$ and lime. In that study, assuming

398 50 L was produced per cow for 42 weeks of lactation, it would cost approximately

399 €30 h^{-1} to spread DSW. Additions of alum, $FeCl_2$ and lime would have negligible

400 impact on this cost. The current study examined the same amendments and found the

401 same order of amendment efficacy as the smaller scale study.

402

403 Amendment of DSW with $FeCl_2$ resulted in low DRP concentrations (Figure 1). The

404 Fe:TP ratio in the $FeCl_2$-amended DWS was much greater than the Al:TP ratio in the

405 alum-amended DSW, and $FeCl_2$ also has a greater solubility than alum. This likely

406 accounted for the marked effect on DRP solubility relative to the alum amendment.

407 Interestingly, DRP losses increased with time interval between application and rainfall

408 for the alum-amended DSW treatment (Figure 1). Over the three rainfall events, DRP

409 comprised 66 % of the TP in runoff from alum-amended DSW. A similar trend was

410 found by Brennan et al. (2011) for alum-amended dairy slurry. This may be due to the

411 "uncommon ion effect" or "salt effect" of alum-amended DSW on the solubility of

412 inorganic phosphates in the soil or to displacement of inorganic orthophosphate

413 anions on soil sorption sites by sulphate anions (Beltman et al., 2000). At 12 h DRP

414 concentration in runoff from the alum treatment was less than the control or

415 unamended DSW treatments, indicating that Al had helped to bind soil and DSW

416 DRP through precipitation and/or co-sorption. However, with greater time to react

417 with the soil, the common ion or sulphate displacement effect of the alum amendment

418 may have counteracted this, leading to increased DRP solubility and losses in runoff.

419

420 **3.3 Suspended sediment in runoff**

421

422 Suspended sediment flux from the control treatment ranged from 13.1 kg ha^{-1} for the

423 12 h time interval to 10.9 kg ha^{-1} for the 48 h time interval, decreasing with increasing

424 time interval (Figure 2). Similar findings were made by other researchers (Regan et

425   al., 2010). The results of the present study were consistent with wetter antecedent soil

426   conditions for the 12 h time interval, leading to more flow over the soil surface,

427 increasing the SS flux in runoff. Analysis of covariance for the relationship between

428 SS and flow volume showed evidence of a linear relationship, but with the slope of

429 the relationship varying between treatments (p=0.01 8). The slopes for alum and FeCl2

430   were not statistically significant, but for DSW, grass and lime, the slopes were all

431   negative with p<0.001.

432

433 Application of unamended DSW did not appear to affect SS losses significantly

434 (Figure 2). As the DM content of the DSW was only 0.2 %, it had little impact on

435   sediment release in surface runoff. The fact that PP losses increased substantially

436   following unamended DSW application (Figure 1), despite little change in SS loss,

437 suggests that DRP in the DSW was rapidly sorbed to surface soil particles which were

438 then mobilised in runoff, as has been suggested above. The correlation between the SS

439 and PP was very weak (the R^2 value was approximately 0.15).

440

441 The chemical amendments were effective at decreasing SS losses from the soil, with

442 decreases of 64 %, 35 % and 34 %, relative to the unamended DSW treatment, for

443   alum, lime and FeCl2, respectively, across the three rainfall events. As the largest part

444 of TP loss from the unamended DSW treatment was PP, this would account for a

445 large portion of the impact of the chemical amendments on P loss, consistent with the

446 observed decrease in PP loss. The fact that alum was most effective at decreasing SS

447   loss, and also PP loss, is consistent with this interpretation. As has been proposed, this

448 is likely due to the release of flocculants (Ca^{2+}, Fe^{2+} and Al^{3+}) into the DSW solution

449 (Brennan et al., 2011), removing PP from suspension and also aiding adhesion of

450 DSW particles and soil particles, thereby decreasing their susceptibility to loss in

451 runoff.

452

453 **4. Conclusions**

454

455 The observed P and sediment losses from this low-P grassland soil following

456 application of unamended DSW indicate the importance of incidental P losses when

457 heavy rain follows shortly after P application and that the current restriction in Ireland

458 of DSW application within 48 h of forecast heavy rainfall is prudent. However, it

459 must be borne in mind that P losses from a runoff box experiment such as this are not

460 quantitative measures of P loss to surface water bodies that might be expected in the

461 landscape for a range of reasons.

462

463 While all three amendments to DSW were effective in decreasing P and SS losses in

464 runoff relative to the unamended DSW treatment, overall, alum was the most

465 effective. The efficacy of these amendments would need to be assessed in field trials

466 and a cost-benefit analysis conducted to further examine whether they could be

467 practically implemented on farms.

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Table 1. Physical and chemical characterisation (± standard deviation) of the grassland soil used in this study (upper 10 cm).

Location	Soil type	Water extractable phosphorus, WEP	Morgan's Phosphorus, Pm	pH	Sand	Silt	Clay	Organic matter, OM
		$mgkg^{-1}$	mgL^{-1}				%	
Co. Galway	Acid Brown Earth	2.3±**0.4**	2.8±**0.5**	6.4±**0.3**	57±**5**	29±**4**	14±**2**	5±**2**
	Cambisol (WRB Classification)							

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	TN	NH$_4$-N	NO$_3$-N	TAN	TP	DRP	pH	DM
	mgL^{-1}							%
Concentration	730	110	2.3	256	14.2	7.3	7.9	0.2
± Standard deviation	212	35	0.5	48	0.5	0.4	0.0	0.1

618 [1] TN = total nitrogen; NH$_4$-N = ammonium-nitrogen; NO$_3$-N = nitrate-nitrogen; TAN
619 = total ammoniacal N; TP = total phosphorus; DRP = total reactive phosphorus; DM
620 = dry matter.

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640 **Figure 1.** Flow-weighted mean concentrations (mg L^{-1}; a) and flux (kg ha^{-1}; b) of

641 dissolved reactive phosphorus (DRP), particulate phosphorus (PP) and dissolved un-

642 reactive phosphorus (DUP) in surface runoff at time intervals of 12, 24 and 48 **h** after
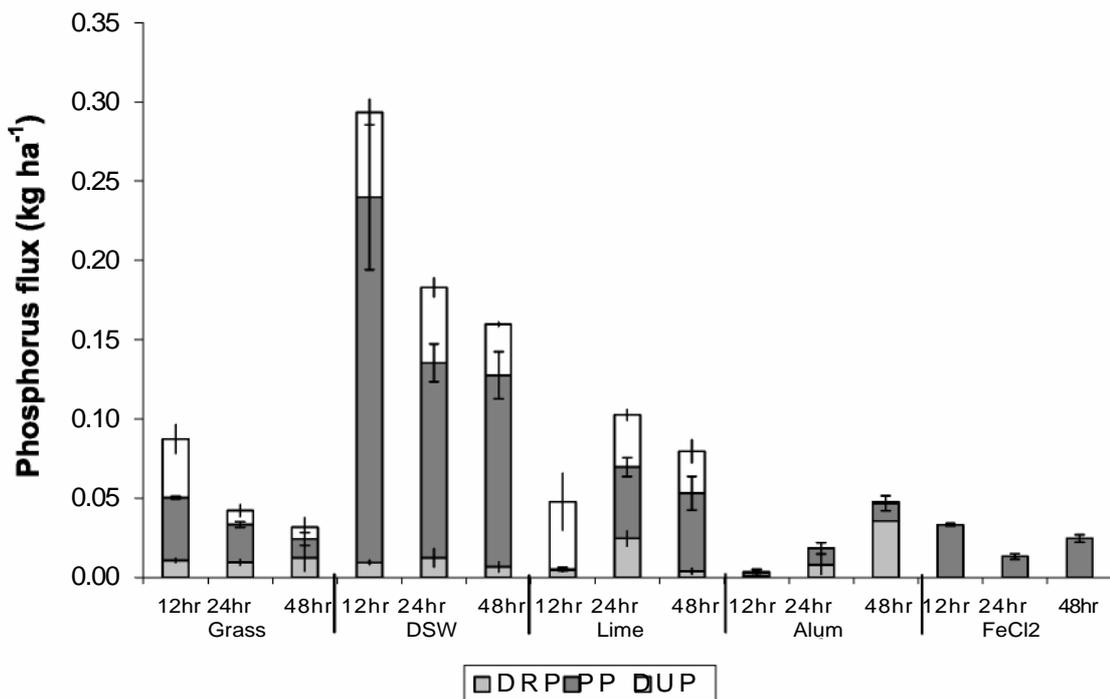
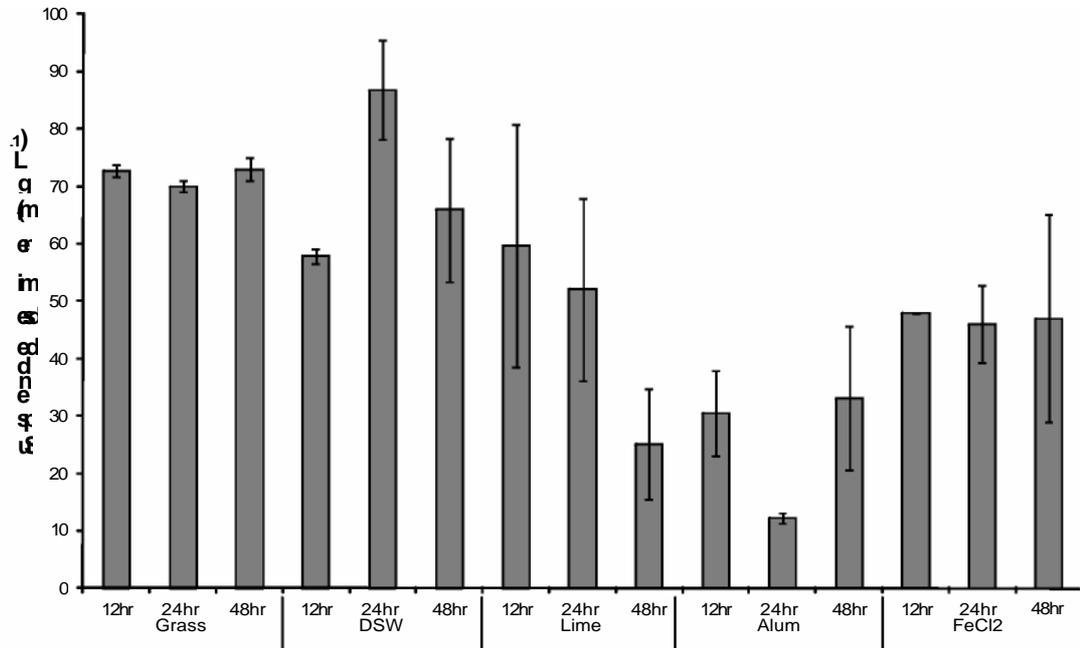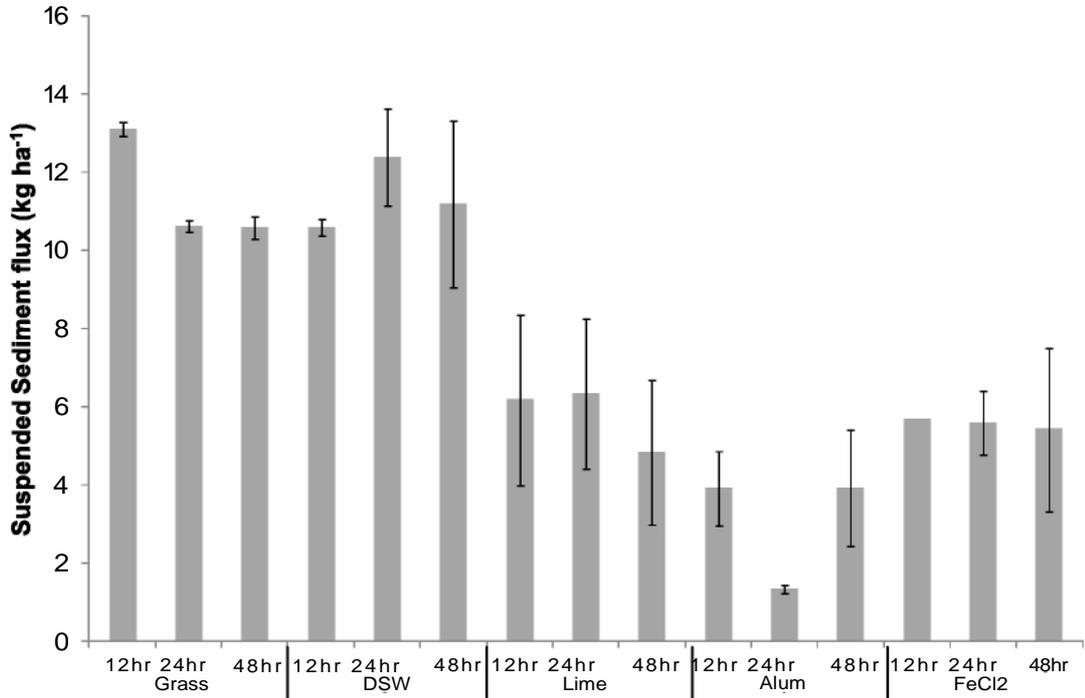643 DSW application to a grassland soil.

644 **a)**
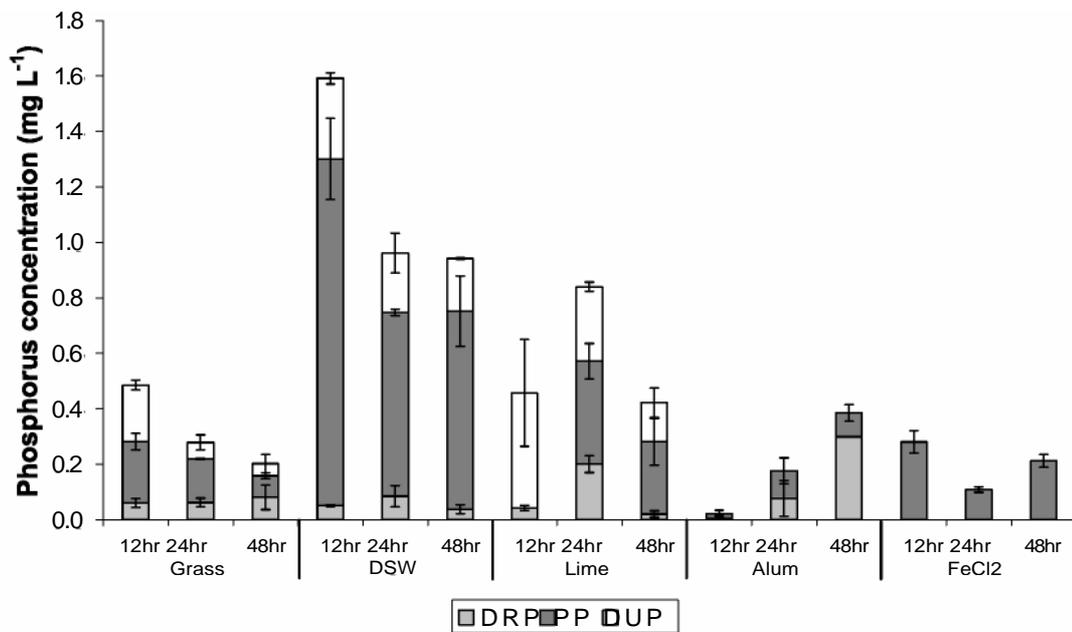
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646 b)

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649 **Figure 2.** Flow-weighted suspended sediment (mg L^{-1}; top graph) and flux (kg ha^{-1};
650 bottom graph) in surface runoff at time intervals of 12, 24 and 48 **h** after DSW
651 application to a grassland soil.

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