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5

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

8

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21

22 **Abstract**

23

24 Dairy soiled water (DSW) is a dilute, low nutrient effluent produced on Irish dairy
25 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 $10.5 \pm 1 \text{ mm h}^{-1}$.
33 Phosphorus concentrations ($1\text{--}1.6 \text{ mg L}^{-1}$) 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**

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 m³ ha⁻¹ over any 42-d period and specifies that it

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), FeCl₂ (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 (P_m; 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 1990a) 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 m³ 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 (NH₄-N), nitrite-N (NO₂-N), nitrate-
148 N (NO₃-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 ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) (alum), (4) analytical grade FeCl_2 , or (5) burnt lime ($\text{Ca}(\text{OH})_2$).

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 $50 \text{ m}^3 \text{ ha}^{-1}$, 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 $10.5 \pm 1 \text{ mm h}^{-1}$ (rainfall with a return period of about 3 y in

200 Ireland; Met Eireann, 2012) and a droplet impact energy of $260 \text{ kJ mm}^{-1} \text{ ha}^{-1}$ 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 $0.45 \mu\text{m}$
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

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 $49 \text{ kg available-P ha}^{-1} \text{ y}^{-1}$. In this study, based on the P content of the
264 DSW (Table 1) and an application rate of $50 \text{ m}^3 \text{ ha}^{-1}$, the soil was loaded at 0.7 kg P
265 $\text{ha}^{-1} \text{ y}^{-1}$.

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 ($14.2 \text{ mg TP L}^{-1}$), 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 ($730 \text{ mg total nitrogen}$
274 $(\text{TN}) \text{ L}^{-1}$) of this DSW was fairly typical (average of $587 \pm 536 \text{ mg L}^{-1}$; Minogue et

275 al., 2010), but the proportion of TN as $\text{NH}_4\text{-N}$ 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 1a. 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 $202 \mu\text{g L}^{-1}$ (0.03 kg ha^{-1}) to $486 \mu\text{g L}^{-1}$
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 hydrolysis (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 FeCl_2 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

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 ($364,000 \text{ mg L}^{-1}$) and iron
394 chloride ($920,000 \text{ mg L}^{-1}$), 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 $\text{€}30 \text{ h}^{-1}$ 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 ($p=0.018$). The slopes for alum and FeCl_2
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 FeCl_2 , 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.

468

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470

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473

474

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

Location	Soil type	Water extractable phosphorus, WEP mg kg ⁻¹	Morgan's Phosphorus, Pm mg L ⁻¹	pH	Sand	Silt	Clay	Organic matter, OM %
Co. Galway	Acid Brown Earth Cambisol (WRB Classification)	2.3±0.4	2.8±0.5	6.4±0.3	57±5	29±4	14±2	5±2

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615

616

617 **Table 2** Water quality characterisation¹ of dairy soiled water used in study (n=3).

	TN	NH ₄ -N	NO ₃ -N	TAN	TP	DRP	pH	DM
	mg L ⁻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; NH₄-N = ammonium-nitrogen; NO₃-N = nitrate-nitrogen; TAN
619 = total ammoniacal N; TP = total phosphorus; DRP = total reactive phosphorus; DM
620 = dry matter.

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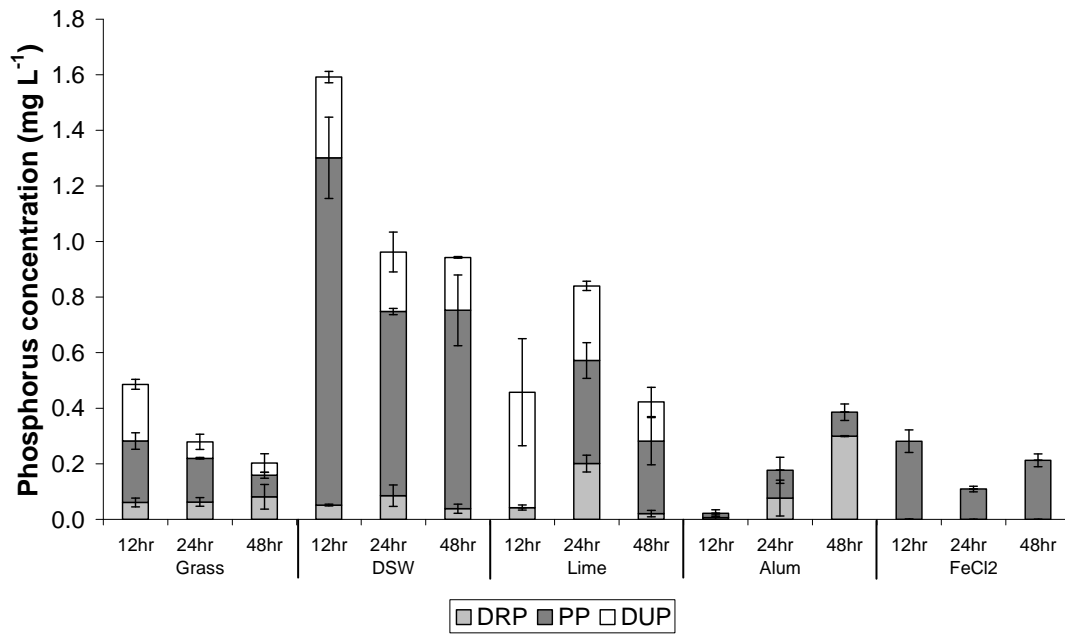
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640 **Figure 1.** Flow-weighted mean concentrations (mg L^{-1} ; a) and flux (kg ha^{-1} ; b) of
 641 dissolved reactive phosphorus (DRP), particulate phosphorus (PP) and dissolved un-
 642 reactive phosphorus (DUP) in surface runoff at time intervals of 12, 24 and 48 h after
 643 DSW application to a grassland soil.

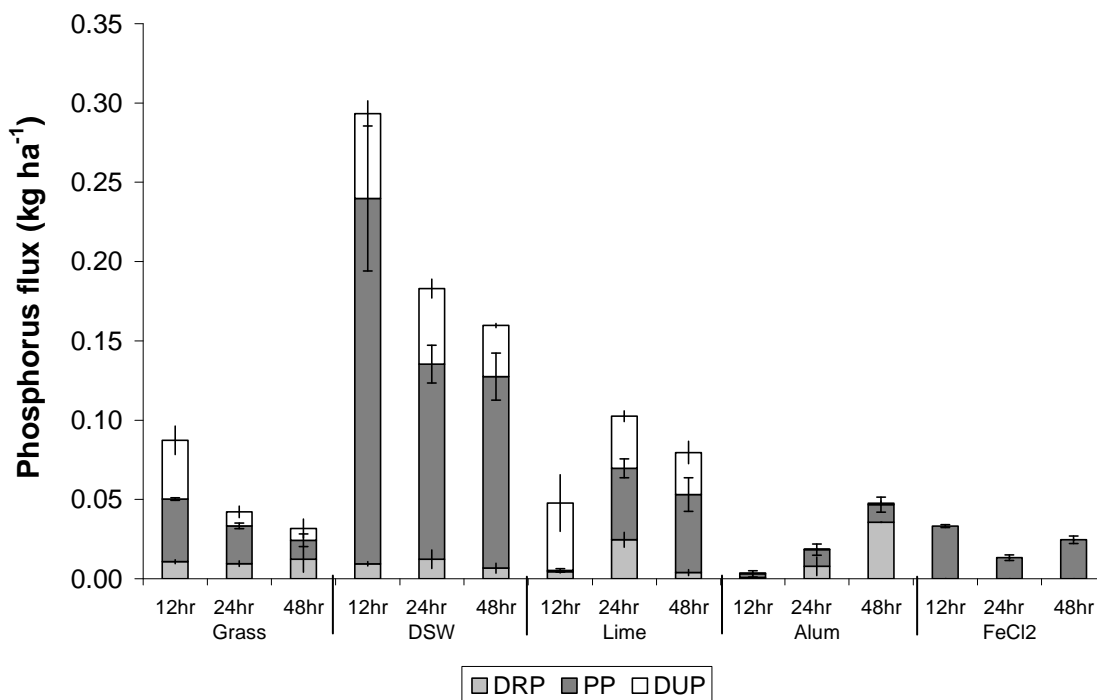
644 a)



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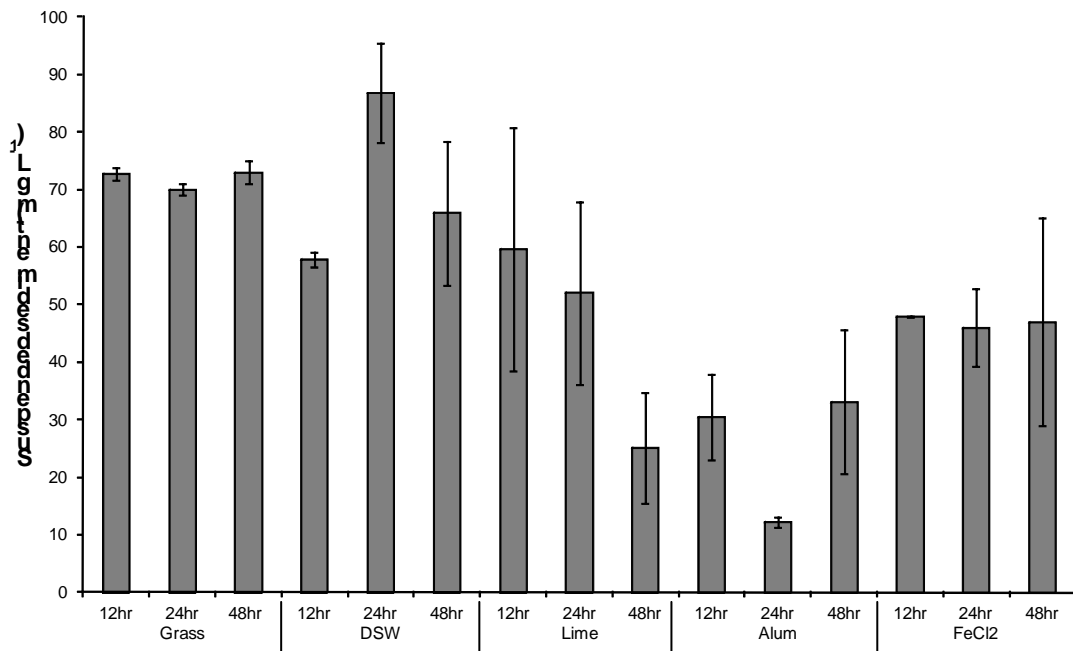
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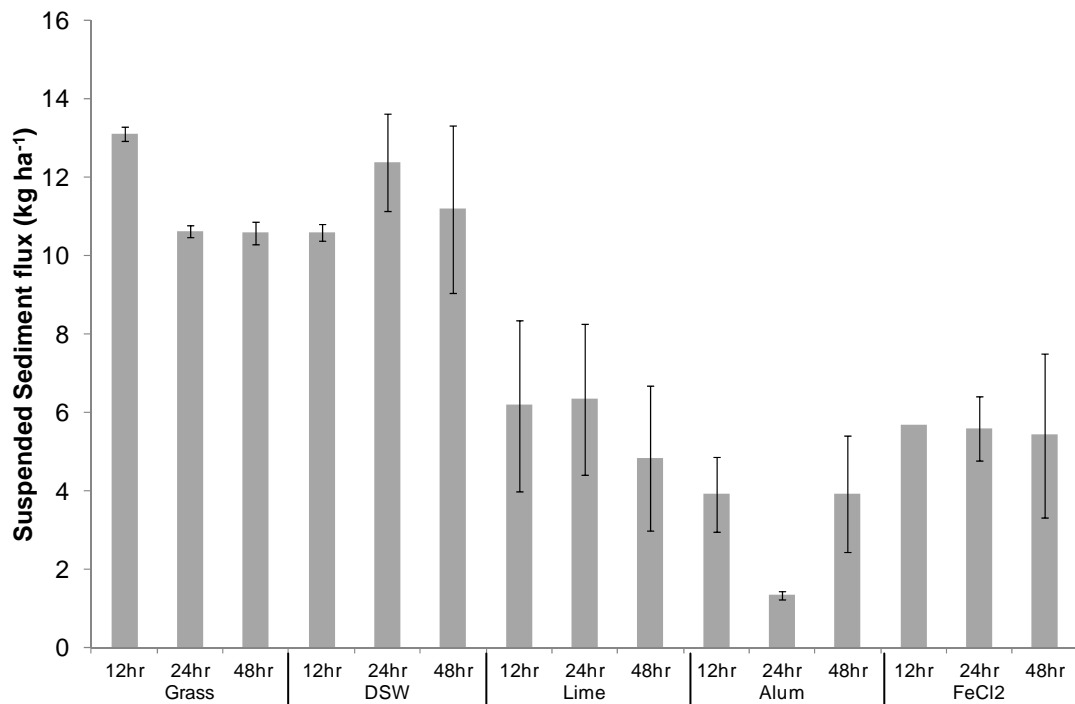
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649 **Figure 2.** Flow-weighted suspended sediment (mg L^{-1} ; top graph) and flux (kg ha^{-1} ;
 650 bottom graph) in surface runoff at time intervals of 12, 24 and 48 h after DSW
 651 application to a grassland soil.

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