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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

Ireland, there is no closed period for the land application of DSW except where heavy rain is forecast within 48 h. Chemical amendments have the potential to decrease phosphorus (P) and suspended sediment (SS) loss from DSW applied to land. This study examined the impact of three time intervals (12, 24 and 48 h) between DSW application and rainfall and five treatments (control, unamended DSW, and DSW amended with lime, alum or ferric chloride ($FeCl_2$)) on P and sediment losses from an intact grassland soil in runoff boxes. Rainfall was simulated at 10.5±1 mm h^{-1}. Phosphorus concentrations (1-1.6 mg L^{-1}) in runoff from DSW application, while not quantitative measures of P loss to surface waters in the field, indicated the importance of incidental P losses and that the current 48 h restriction in Ireland is prudent. Unamended DSW application increased P loss by, on average, 71 %, largely due to an increase in particulate phosphorus (PP) loss. All three amendments were effective in decreasing P and SS losses in runoff and, apart from the SS results for lime, were significantly different ($p<0.05$) to the control at at least one time point. Lime (a 64 % reduction in total phosphorus (TP) in comparison with DSW only) was less effective than alum or $FeCl_2$, likely due to the lower solubility of $CaCO_3$ in water. Chemical amendment showed potential to decrease P losses from land application of DSW, but the efficacy of such amendments would need to be assessed in field trials and a cost-benefit analysis conducted to further examine whether they could be practically implemented on farms.

Keywords: Dairy soiled water; farm effluent; application timing; incidental loss; chemical amendment.

1. Introduction

Livestock production based on grazed grassland is associated with inputs of nitrogen (N) and phosphorus (P) to soils, including dung and urine deposition, chemical fertilizers, and organic fertilizers (manures and slurries). Dairy soiled water (DSW) is one such organic fertilizer on dairy farms. It consists of wash-water from the milking parlour and holding areas for livestock, which contains parlour washings, livestock faeces and urine. In Ireland, DSW is defined as a wastewater with a 5-d biochemical oxygen demand (BOD_5) of less than 2,500 mg L^{-1} and a dry matter (DM) content of less than 1 % (SI 610 of 2010), distinguishing it from more concentrated cattle slurries. Dairy soiled water is generated every d on dairy farms and can be highly variable in composition. Martínez-Suller et al. (2010) found that, due to management practices, BOD_5 can reach as high as 8,400 mg L^{-1} and DM can be far in excess of 1 %. However, in a survey of 60 Irish dairy farms over a year, Minogue et al. (2010) found that mean BOD_5 concentration was 2,246 mg L^{-1} and mean DM was 0.5 %, and most samples were below the BOD_5 and DM limits. Application to land is the most common method for disposal of DSW, as it has a high nitrogen fertilizer replacement value (Minogue et al., 2011). However, there is a risk of nutrient (N and P) loss associated with land application of all types of slurries and DSW (Di et al., 1998; Woodard et al., 2002; Withers and Bailey, 2003; Ryan et al., 2006), particularly incidental P losses in runoff, when rainfall events follow shortly after P application to the soil. Such incidental losses can account for a large portion of P loss from agricultural fields (Sharpley and Tunney, 2000).

The Statutory Instrument (SI) governing the application of DSW to land in Ireland (SI 610 of 2010) limits application at 50 m^3 ha^{-1} over any 42-d period and specifies that it cannot be applied to land if heavy rain is forecast within 48 h of application. Unlike more concentrated cattle slurries, DSW is not subject to a ‘closed period’ for application in the winter months when soils tend to be wet and heavy rainfalls associated with Atlantic depressions occur. It can be very difficult to forecast rain events in Ireland, particularly in winter months, and application is likely to occur at time intervals shorter than 48 h before heavy rain in some instances. No study has, to date, examined the impact of short time durations between DSW application and surface runoff of nutrients and suspended sediment (SS). Potential methods to mitigate nutrient and SS loss in runoff when rainfall occurs at these time intervals also warrant investigation.

The potential of chemical amendments, such as lime, gypsum, alum and ferric chloride, to decrease P loss from soils has been investigated by numerous researchers (e.g. Callahan et al., 2002; Zvomuya et al., 2006; Murphy and Stevens, 2010). There has also been some investigation of the impacts of amendments to agricultural wastewaters, in particular, manure (Kalbasi and Karthikeyan, 2004; Brennan et al., 2011) or poultry litter (Moore and Edwards, 2005), on surface runoff of nutrients, metals and SS. These and other studies reported that there was no increased risk of heavy metal release to runoff water, following chemical amendment of poultry litter or agricultural wastewaters (Moore et al., 1998; Edwards et al., 1999; Brennan et al., 2011). However, little work has been conducted on DSW (Fenton et al., 2011). The mode of addition of chemicals to wastewater may vary between incorporation into soil (Novak and Watts, 2005; Murphy, 2007), direct addition to manure (Moore et al., 1998), or addition after application of manure to land (Torbert et al., 2005). Brennan et al. (2011) found that poly-aluminum chloride hydroxide (PAC), added at 0.93:1

aluminum (Al):total phosphorus (TP) of slurry, reduced dissolved reactive phosphorus (DRP) by up to 86 %, compared with the surface runoff from dairy cattle slurry alone; while alum, added at 1.11:1 Al:TP of slurry, was most effective in reducing SS (88 %), TP (94 %), particulate phosphorus (PP) (95 %), total dissolved phosphorus (TDP) (81 %), and dissolved un-reactive phosphorus (DUP) (86 %). Fenton et al. (2011) investigated the use of chemical amendments to reduce P losses arising from the land application of DSW to grassland in a desk-scale experiment and found that the most effective chemicals were alum (72 % reduction), $FeCl_2$ (89 % reduction) and lime (83 % reduction). Therefore, these three amendments were selected for further study in the present laboratory runoff experiment.

The aim of the present study was to examine the effect of (1) high intensity rainfall events after 12, 24 and 48 h of land application of DSW to grassland, and (2) chemical amendment of DSW on losses of P and SS in runoff.

2. Materials and Methods

Intact 0.1 m-deep and 0.5 m-long soil cores were collected from grassland, which had not received fertiliser applications for more than 10 y, in Galway City, Republic of Ireland (53°16’N, 9°02’ W). Soil cores (n=3) taken to a depth of 0.1 m below the ground surface from the same location, were air dried at 40 °C for 72 h, crushed to pass a 0.002 m sieve, and analysed for Morgan’s P (Pm; the national test used for the determination of plant available P in Ireland) using Morgan’s extracting solution (Morgan, 1941). Water extractable phosphorus (WEP) was measured by shaking 0.5 g of soil in 40 ml of distilled water for 1 h, filtering (0.45 µm) the supernatant water and determining P colorimetrically. The soil cores were kept separate for analysis and replication (n=3) was used in analysis of each of the 3 cores. Soil pH (n=3 from each of the soil cores) was determined using a pH probe and a 2:1 ratio of deionised water-to-soil. Particle size distribution (PSD) was determined using B.S.1377-2:1990 (BSI, 1990a) and the organic matter content of the soil was determined using loss on ignition (B.S.1377-3; BSI, 1990b).

2.1 Dairy soiled water sampling and analysis

Dairy soiled water produced from the concrete holding areas (non-scraped) and milking parlour washings of 137 spring calving dairy cows (milked twice daily) at the Environmental Research Centre (Teagasc, Wexford), was collected in March, 2011. High pressure hoses were used to clean the yards. There were three tanks, connected in series, with a total capacity of approximately 52 m^3 and a working capacity of approximately 80 %. The tanks were agitated for 20 min until the DSW was homogenized, and DSW was collected in a 10-L plastic drum and transported to the laboratory in a temperature-controlled container within one d of sample collection. The DSW was stored at 4 °C until immediately prior to the start of the experiment (about 2 d after sample collection). The sample was fully analysed colorimetrically for the following water quality parameters using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland) (each tested at n=3 and, with the exception of TP, filtered through a 0.45 µm filter): ammonium-N (NH_4-N), nitrite-N (NO_2-N), nitrate-N (NO_3-N), total ammoniacal N (TAN), DRP and TP (after acid persulphate digestion) in accordance with the standard methods (APHA, 2005). To test for TAN, 50 ml of DSW was diluted in 1 L 0.1M HCl and then tested in the nutrient analyser.

pH was measured using a pH probe (WTW SenTix 41 probe with a pH 330 meter, WTW, Germany) and the DM content was determined by drying at 40°C for 72 h.

2.2 Experimental treatments

The five treatments examined in this study were: (1) control (grassed soil only), (2) unamended DSW, and DSW amended with either (3) aluminium sulphate 18-hydrate ($Al_2(SO_4)_3.18H_2O$) (alum), (4) analytical grade $FeCl_2$, or (5) burnt lime ($Ca(OH)_2$). Amendments were applied at stoichiometric ratios determined from Fenton et al. (2011). Alum was applied at a rate of 8.8:1 (Al:TP), ferric chloride at a rate of 200:1 (Fe:TP), and lime at a rate of 2,500:1 (Ca:TP). Amendments were added to the DSW and mixed rapidly (10 min at 100 rpm) using a jar test flocculator immediately prior to application to runoff boxes. The temperature of the laboratory in which the experiments were conducted was approximately 10 ^{o}C. Two replicates of each treatment were subject to rainfall at a time interval between treatment application and rainfall of either 12, 24 or 48 h, giving a total of 30 runoff boxes (5 treatments x 3 time intervals x 2 replicates). The limited replication involved (n=2) was due to limited availability of soil samples from the study site and, in order to take this into account, the formal inference was conducted in an exploratory manner rather than as evidence of cause and effect as would be normal for a designed experiment. Relationships identified were taken as indicating association only.

2.3 Runoff boxes and rainfall simulation set-up

This experiment used two laboratory runoff boxes, 1-m-long by 0.225-m-wide by 0.05-m-deep with side walls 0.025 m higher than the soil surface and 0.005-m-diameter drainage holes each located at 0.3-m-intervals along the base (after Regan et al., 2010). The runoff boxes were positioned at an angle of 5 degrees to the horizontal and all surface runoff was collected with an overflow weir, positioned at the same level as the soil surface, and a funnel. Cheese cloth was placed at the base of each runoff box before placing the soil cores. Intact grassed cores from the study site were transported to the laboratory and stored at 11°C in a cold room prior to testing. All experiments were carried out within 14 d of soil core collection. Immediately prior to the start of each runoff box experiment, the cores were trimmed and placed in the runoff box. Each core was butted against its adjacent core to form a continuous surface. Molten candle wax was used to seal any gaps between the cores and the sides of the runoff box.

The packed cores were then saturated until ponding occurred on the soil surface using a rotating disc, variable-intensity rainfall simulator (after Williams et al., 1997), and left to drain for 24 h before the experiment commenced. All soils were approximately at field capacity prior to the start of each experiment. Dairy soiled water and amended DSW were applied to the surface of the intact grassland soil in runoff boxes at a rate equivalent to 50 m^3 ha^{-1}, the legal limit for application in any 42-d period. The DSW and chemically-amended DSW were spread evenly across the soil surface.

The rainfall simulator consisted of a single 1/4HH-SS14SQW nozzle (Spraying Systems Co., Wheaton, IL) attached to a 4.5-m-high metal frame, and calibrated to achieve an intensity of 10.5±1 mm h^{-1} (rainfall with a return period of about 3 y in

Ireland; Met Eireann, 2012) and a droplet impact energy of 260 kJ mm^{-1} ha^{-1} at 85 % uniformity. During each rainfall simulation, the drainage holes were sealed to replicate conditions of saturation excess runoff. Significant surface runoff (determined once consistent, continuous droplets of water flowed from the flume) typically began within 20-30 min. Runoff was collected for this initial period and then 5, 10, 15, 20, 25, 30, 40, 50 and 60 min thereafter. The volume of water collected during each time interval was measured and collection of runoff ceased at the 60-min sampling interval. The water used in the rainfall simulations was tap water, which had a DRP concentration of less than 0.005 mg L^{-1}, a pH of 7.7±0.2 and an electrical conductivity (EC) (measured using a LF 96 Conductivity Meter, WTW, Germany) of 0.435 dS m^{-1}. The calcium (Ca^{2+}) concentration of the tap water, measured by atomic absorption spectrophotometry (AAS), was 3.11 mg L^{-1} and was higher than the annual mean concentration of Ca^{2+} in rainwater (0.85 mg L^{-1}) measured between 1992 and 1994 for Ireland (Jordan, 1997). This may have impacted somewhat on measurements, but owing to availability, the same source has been used in similar experiments (Regan et al., 2010). Water pH was measured immediately prior to each event using a pH and electrical conductivity meter.

2.4 Runoff analysis

Immediately after collection, runoff water samples were passed through a 0.45 µm filter and a subsample was analysed colorimetrically for DRP. A second filtered sample was analysed for TDP using acid persulphate digestion (APHA, 2005), followed by spectrophotometry using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland) after Murphy and Riley (1962). Unfiltered runoff water samples were also collected and TP was measured using acid persulphate digestion, followed by spectrophotometry. Total P comprised PP and TDP, with TDP consisting of DRP and DUP. Particulate phosphorus was calculated by subtracting TDP from TP. Suspended solids were determined for all samples by vacuum filtration of well-mixed runoff water through Whatman GF/C (pore size: 1.2 µm) filter paper. All samples were tested in accordance with the Standard Methods (APHA, 2005). All reported concentrations in this paper were flow-weighted mean concentrations (FWMC) calculated based on surface runoff volume, collected in each time interval, and the measured concentrations.

2.5 Statistical Analysis

The analysis was conducted as an ANOVA of the factorial combinations of treatment and time. There were five levels of treatment (control, unamended DSW, lime, $FeCl_2$ and alum) and three levels of the time factor (12, 24 and 48 h). Due to the limited replication, it was not feasible to account for all structural effects in the experiment. Large differences in variance between treatments were taken into account in a heterogeneous variance mixed model using the Mixed procedure of SAS (2009). The repeated measures aspect of the experiment was not modelled. Tukey adjustments were made to account for multiplicity in comparison of means. Pearson product-moment correlations were used to examine association between PP and SS. The relationship between SS and volume was examined using analysis of covariance, regressing SS and other relevant variables on volume. Residual checks showed no evidence that the distributional assumptions of the analysis were not met.

3. Results and Discussion

3.1 Soil and dairy soiled water characterisation

The characteristics of the soil and DSW used in this study are tabulated in Tables 1 and 2, respectively. The grassland sandy loam soil used in this study was a well-drained sandy loam Acid Brown Earth (WRB classification: Cambisol). The soil pH, at 6.4, was optimal for grass growth and P plant-availability. It had a relatively low Morgan's P concentration of 2.8 mg L^{-1}. This soil would be classified as an Index 1 soil in the Irish grassland soil P index system (SI 610 of 2010) and would therefore not be perceived as being a high risk for P loss to water in terms of its P content. Agronomic advice to increase grass production would be to apply additional P to this soil in order to build up soil reserves of P. This soil could receive P at rates up to a maximum of 49 kg available-P ha^{-1} y^{-1}. In this study, based on the P content of the DSW (Table 1) and an application rate of 50 m^3 ha^{-1}, the soil was loaded at 0.7 kg P ha^{-1} y^{-1}.

Dairy soiled water used in the study had a DM content of 0.2 % (Table 2). This would place it within the legally defined threshold for soiled water of 1 % DM and at the more dilute end of the range of DSW concentrations found on Irish farms (average of 0.5 %; Minogue et al., 2010). In terms of P content (14.2 mg TP L^{-1}), this DSW was also relatively dilute (average of 80 mg L^{-1}; Minogue et al., 2010). The proportion of TP as DRP, at 51 %, was typical of DSW composition on Irish dairy farms. The bulk of the remaining TP was likely in organic form. The N content (730 mg total nitrogen (TN) L^{-1}) of this DSW was fairly typical (average of 587 ± 536 mg L^{-1}; Minogue et al., 2010), but the proportion of TN as NH_4-N was relatively low (15 %, compared to 36 %).

3.2 Phosphorus loss in runoff

The FWMC of P speciation for the control (grass only), DSW only, and amended DSW treatments for all three rainfall events are presented in Figure 1a. The interaction of time and treatment was significant for DRP, TP, PP and SS ($P < 0.001$). Generally, the highest concentrations of P in runoff occurred during the first 20 min of the commencement of runoff, before reaching steady state. Mean TP concentrations in surface runoff from the control ranged from 202 µg L^{-1} (0.03 kg ha^{-1}) to 486 µg L^{-1} (0.09 kg ha^{-1}) (Figure 1). Most of this P was present in dissolved un-reactive form (44 %) or particulate form (36 %), whereas only 20 % was in dissolved reactive form. The results indicated that P concentrations in surface runoff water from a low P index soil such as this may exceed the maximum allowable concentration (MAC) for discharge to receiving waters of 0.03 mg L^{-1} (2000/60/EC: Council of the European Union, 2000), despite its low P content.

It must be borne in mind that this experiment only assessed P loss in runoff from an isolated 0.225 m^2 area of soil with a relatively steep slope, relatively intense and persistent rainfall, and with no capacity to drain water vertically (saturation excess runoff). In the field, rainfall would typically be less intense and persistent, and the soil would typically have the capacity for vertical drainage. Therefore, the experiment replicated a worst-case scenario in terms of potential incidental P loss from soil. In small-scale experiments, the attenuation of contaminants during transport is limited.

Therefore, while P losses from the runoff boxes may be used to judge the relative merit of chemical amendments and the effects of time interval, they are not quantitative measures of P loss to surface water bodies that might be expected in the landscape.

Application of un-amended DSW increased concentrations of TP in runoff significantly (Figure 1) to 1.6 mg L^{-1} (total loss of 0.3 kg ha^{-1}) for the 12-h rainfall event ($p<0.0001$), 0.96 (total loss of 0.18 kg ha^{-1}) for the 24-h event ($p<0.008$) and 0.94 mg L^{-1} (total loss of 0.16 kg ha^{-1}) for the 48-h event ($p<0.0017$). This highlights the potential importance of incidental P losses when heavy rain follows soon after application of a P source to soil, with TP losses being over three times greater than the control at 12 h.

Total P concentrations in runoff from both the control and unamended DSW treatments tended to decrease with time interval between treatment application and rainfall (Figure 1). This decrease in concentration was coincident with a decrease in runoff volume (e.g. from 4,057 to 3,414 to 3,266 ml for the 12, 24 and 48 h time intervals, respectively, for the control treatment). It would appear that, due to a longer time draining before rainfall was initiated (36, 48 and 60 h after saturation for the 12, 24 and 48 h time intervals, respectively), antecedent soil moisture conditions were different, giving the longer time interval soils a greater capacity to infiltrate and store rainfall. The higher soil water content and lower infiltration and storage capacity of the 12 h time interval soils may have forced more of the water to flow directly over the soil surface, mobilising P that is typically concentrated in the upper surface of grassland soils. The soil used in the runoff boxes came from the top 5 cm of the soil profile and will have a higher concentration than the top 10 cm of soil as shown in Table 1. This mechanism would be consistent with greater concentrations of PP in runoff from the 12 h treatment (Figure 1) as PP loss is associated with water flow over the soil surface and it is the uppermost surface soil that influences the concentration of P in surface runoff most (Sharpley, 1980).

As the proportional decrease in P concentrations with time interval was similar for both the control and the unamended DSW treatments, due to antecedent soil moisture conditions, it seems unlikely that there was any effect of time interval between DSW application and rainfall on P loss. This suggests that the measures in SI 610 of 2010 restricting DSW application when heavy rain is forecast within 48 h are prudent to decrease the potential for pollution of receiving waters. It is, of course, likely that as the time interval between application and heavy rain widens further, P losses are likely to decrease due to further interaction with the soil and plant uptake.

As with the control, DRP concentrations in runoff from the unamended DSW treatment were relatively low (Figure 1). Despite DRP making up 51 % of TP in the DSW, most of the increase in TP concentrations relative to the control was due to increased PP and DUP loss (Figure 1). Particulate P constituted 75 % of the total mass of P released over the three rainfall events. Usually the predominance of dissolved forms of P in runoff reflects particle retention by the vegetation and limited erosion due to vegetative cover and the absence of livestock (Haygarth et al., 1998; Hart et al., 2004). It is likely that DRP in DSW was sorbed rapidly by the soil (Maguire et al., 2001), while PP may have been more susceptible to mobilisation and loss at the soil surface (Regan et al., 2010). Given that the PP content of DSW is typically quite low

(Minogue et al., 2010), it would seem likely that DRP added in the DSW may have sorbed to soil particles which were then lost in runoff.

Dissolved un-reactive phosphorus concentrations in runoff from the unamended DSW treatment were also higher than the control. This probably reflects mobilisation of DUP added in the DSW (Brennan et al., 2011). The DUP fraction is generally considered to consist largely of dissolved organic P (Toor et al., 2003; Murphy et al., 2010). This organic P is generally not as bioavailable as reactive forms, but can become bio-available and contribute to eutrophication in receiving water bodies through chemical or enzymatic hydrolisation (Correll, 1998)

All three amendments to DSW were effective in decreasing P concentrations in runoff relative to the unamended DSW treatment (Figure 1). Lime decreased the FWMC of TP (average across the three rainfall events) by 66 % ($p<0.07$), whereas alum and $FeCl_2$ were more effective, decreasing concentrations by 84 ($p<0.005$) and 83 % ($p<0.007$), respectively. For all three amendments, most of the decrease in TP loss was due to a decrease in PP and DUP loss relative to the unamended DSW treatment. This is most likely due to the fact that all three amendments release effective flocculants (Ca^{2+}, Fe^{2+} and Al^{3+}) into the DSW solution, leading to flocculation and removal of PP and DUP from suspension (Brennan et al., 2011). These flocculants may also aid adhesion of particles in the DSW to soil particles and adhesion of soil particles themselves, further decreasing P losses in runoff (Brennan et al., 2011).

Lime was less effective than the other two amendments, largely due to high losses of DUP relative to both the unamended DSW treatment and the control. The lime amendment increased the pH of surface runoff, giving an average pH of 8.9±0.13 across the three rainfall events, while the other amendments produced surface runoff with a pH similar to that of the unamended DSW treatment (6.9±0.14). Liming is often associated with an initial flush of soluble organic matter and dissolved organic P release that can increase P losses in runoff or leachate, at least temporarily (Murphy, 2007). At the higher pH of the limed DSW treatment, organic P can be more soluble due to desorption or dispersion of organic matter, or release of organic P through increased microbial activity (Hannapel et al., 1964). Dissolved un-reactive phosphorus made up a greater proportion of TP for the lime amendment than the other two chemically amended DSW treatments. Most of the DUP in runoff is likely to be dissolved organic P. Lime also increased DRP losses relative to the control and unamended DSW treatment for the 24-h rainfall event. Such inconsistent effects of lime on DRP solubility have been found by others (Murphy and Stevens, 2010).

Alum and $FeCl_2$ were also more effective than lime in decreasing PP loss ($p<0.05$) despite the fact that the Ca:TP stoichiometric ratio in the lime-amended DSW (2,500:1) was much greater than the Al:TP ratio in the alum treatment (8.8:1) and the Fe:TP ratio in the $FeCl_2$ treatment (200:1). This is likely due to the lower solubility of $CaCO_3$ in water (15 mg L^{-1}) than aluminium sulfate (364,000 mg L^{-1}) and iron chloride (920,000 mg L^{-1}), delivering concentrations of flocculant four orders of magnitude less. In a desk-scale experiment examining the feasibility of alum, $FeCl_2$ and lime to decrease P loss from land application of DSW, Fenton et al. (2011) found that alum was the most feasible, followed by $FeCl_2$ and lime. In that study, assuming 50 L was produced per cow for 42 weeks of lactation, it would cost approximately €30 h^{-1} to spread DSW. Additions of alum, $FeCl_2$ and lime would have negligible impact on this cost. The current study examined the same amendments and found the same order of amendment efficacy as the smaller scale study.

Amendment of DSW with $FeCl_2$ resulted in low DRP concentrations (Figure 1). The Fe:TP ratio in the $FeCl_2$-amended DWS was much greater than the Al:TP ratio in the alum-amended DSW, and $FeCl_2$ also has a greater solubility than alum. This likely accounted for the marked effect on DRP solubility relative to the alum amendment. Interestingly, DRP losses increased with time interval between application and rainfall for the alum-amended DSW treatment (Figure 1). Over the three rainfall events, DRP comprised 66 % of the TP in runoff from alum-amended DSW. A similar trend was found by Brennan et al. (2011) for alum-amended dairy slurry. This may be due to the "uncommon ion effect" or "salt effect" of alum-amended DSW on the solubility of inorganic phosphates in the soil or to displacement of inorganic orthophosphate anions on soil sorption sites by sulphate anions (Beltman et al., 2000). At 12 h DRP concentration in runoff from the alum treatment was less than the control or unamended DSW treatments, indicating that Al had helped to bind soil and DSW DRP through precipitation and/or co-sorption. However, with greater time to react with the soil, the common ion or sulphate displacement effect of the alum amendment may have counteracted this, leading to increased DRP solubility and losses in runoff.

3.3 Suspended sediment in runoff

Suspended sediment flux from the control treatment ranged from 13.1 kg ha^{-1} for the 12 h time interval to 10.9 kg ha^{-1} for the 48 h time interval, decreasing with increasing time interval (Figure 2). Similar findings were made by other researchers (Regan et al., 2010). The results of the present study were consistent with wetter antecedent soil conditions for the 12 h time interval, leading to more flow over the soil surface, increasing the SS flux in runoff. Analysis of covariance for the relationship between SS and flow volume showed evidence of a linear relationship, but with the slope of the relationship varying between treatments ($p=0.018$). The slopes for alum and $FeCl_2$ were not statistically significant, but for DSW, grass and lime, the slopes were all negative with $p<0.001$.

Application of unamended DSW did not appear to affect SS losses significantly (Figure 2). As the DM content of the DSW was only 0.2 %, it had little impact on sediment release in surface runoff. The fact that PP losses increased substantially following unamended DSW application (Figure 1), despite little change in SS loss, suggests that DRP in the DSW was rapidly sorbed to surface soil particles which were then mobilised in runoff, as has been suggested above. The correlation between the SS and PP was very weak (the R^2 value was approximately 0.15).

The chemical amendments were effective at decreasing SS losses from the soil, with decreases of 64 %, 35 % and 34 %, relative to the unamended DSW treatment, for alum, lime and $FeCl_2$, respectively, across the three rainfall events. As the largest part of TP loss from the unamended DSW treatment was PP, this would account for a large portion of the impact of the chemical amendments on P loss, consistent with the observed decrease in PP loss. The fact that alum was most effective at decreasing SS loss, and also PP loss, is consistent with this interpretation. As has been proposed, this is likely due to the release of flocculants (Ca^{2+}, Fe^{2+} and Al^{3+}) into the DSW solution (Brennan et al., 2011), removing PP from suspension and also aiding adhesion of

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

4. Conclusions

The observed P and sediment losses from this low-P grassland soil following application of unamended DSW indicate the importance of incidental P losses when heavy rain follows shortly after P application and that the current restriction in Ireland of DSW application within 48 h of forecast heavy rainfall is prudent. However, it must be borne in mind that P losses from a runoff box experiment such as this are not quantitative measures of P loss to surface water bodies that might be expected in the landscape for a range of reasons.

While all three amendments to DSW were effective in decreasing P and SS losses in runoff relative to the unamended DSW treatment, overall, alum was the most effective. The efficacy of these amendments would need to be assessed in field trials and a cost-benefit analysis conducted to further examine whether they could be 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
		mg kg^{-1}	mg L^{-1}		%			
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**

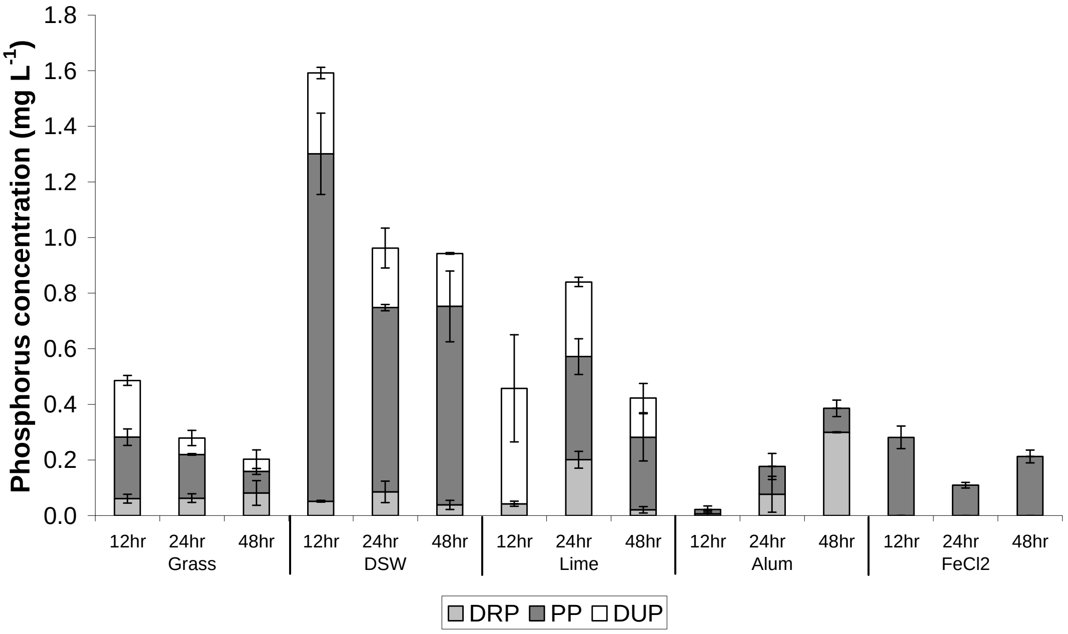
Table 2 Water quality characterisation[1] of dairy soiled water used in study (n=3).

	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

[1] TN = total nitrogen; NH_4-N = ammonium-nitrogen; NO_3-N = nitrate-nitrogen; TAN = total ammoniacal N; TP = total phosphorus; DRP = total reactive phosphorus; DM = dry matter.

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

a)



b)

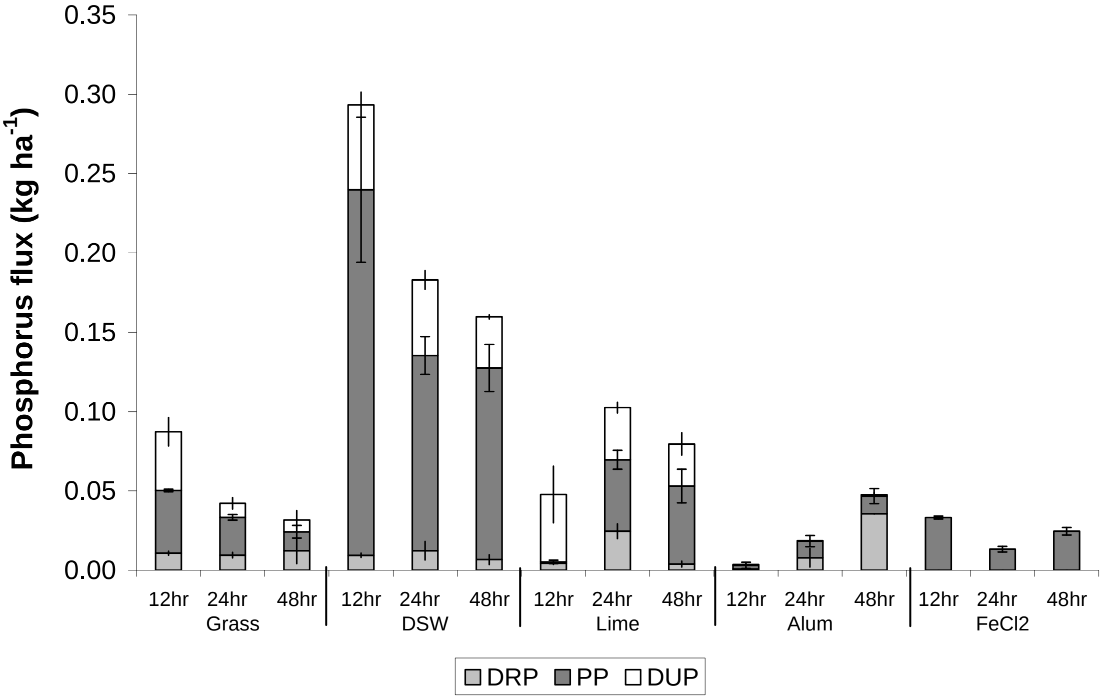


Figure 2. Flow-weighted suspended sediment (mg L^{-1}; top graph) and flux (kg ha^{-1}; bottom graph) in surface runoff at time intervals of 12, 24 and 48 **h** after DSW application to a grassland soil.