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

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## Abstract

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

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

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

## Introduction

Land application of dairy cattle slurry can result in incidental and chronic phosphorus (P) losses to a waterbody (Buda et al., 2009), which may lead to eutrophication (Carpenter et al., 1998). Incidental P losses take place when a rainfall event occurs shortly after slurry application and before slurry infiltrates the soil, while chronic P losses are a long-term loss of P from soil as a result of a build-up in soil test P (STP) caused by application of inorganic fertilisers and manure (Buda et al., 2009). Incidental P losses arising from rainfall events following land application of dairy cattle slurry are the focus of this study.

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

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

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

Chemical amendment of slurry using aluminium (Al), iron (Fe), or calcium (Ca) based compounds reduce P solubility in manure (Dao, 1999; Dou et al., 2003; Kalbasi and Karthikeyan, 2004) and reduce P in runoff from plots receiving alum amended poultry litter (Moore and Edwards, 2005) with negligible effect on metal loss (McFarland et al., 2003). Chemical amendments reduce incidental P losses by a combination of the formation of stable metal-phosphorus precipitates (such as Al-P phosphates in the case of alum) and flocculation of the particles in the slurry to form larger particles, which are less prone to erosion (Tchobanoglous et al., 2003). Previous studies have found that there was no risk of increased metal release posed by chemical amendment of poultry litter (Moore et al., 1998), dirty water (McFarland et al., 2003), or horse manure (Edwards et al., 1999). The present study examines the effect of chemical amendment of dairy cattle slurry on both P and metal (namely Al, Fe and Ca) losses to runoff. Previous studies have only examined the effect of amendments on P solubility (Dao, 1999; Dao and Daniel, 2002; Dou et al., 2003).

Chemical amendments can be incorporated into soil to reduce soluble P in soils with high STP (Novak and Watts, 2005), added directly to the manure before land application (Moore et al., 1998), or applied after manure application to reduce P losses in runoff (Torbert et al., 2005). Chemical amendment of poultry litter has been proven to be effective in reducing P losses from poultry litter in the U.S.A. and has been used there for over 30 years (Moore and Edwards, 2005). However, there has been limited work involving chemical amendment of dairy manure (Dao, 1999; Dou et al., 2003; Kalbasi and Karthikeyan, 2004). In an incubation study, Dou et al. (2003) found that technical grade alum, added at 0.1 kg/kg (kg alum per kg slurry) and 0.25 kg/kg, reduced WEP in swine and dairy slurry by 80% and 99%, respectively. Dao (1999) amended farm yard manure with caliche, alum and flyash in an incubation experiment, and reported WEP reductions in amended manure compared to the control of 21, 60 and 85%, respectively. Kalbasi and Karthikeyan (2004) applied untreated and amended dairy slurry to a soil and incubated it for 2 years; alum and $FeCl_2$ were observed to decrease P solubility, while lime amendments increased WEP.

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

## 2. Materials and Methods

### 2.1. Soil sample collection and analysis

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

### 2.2. Slurry collection and analysis

Cattle slurry from dairy replacement heifers was taken from a farm (53°18’ N, 8°47’ W) in County Galway, Republic of Ireland in Winter (February), 2010. The storage tanks were agitated and slurry samples were transported to the laboratory in 10-L drums. Slurry samples were stored at 4°C. Slurry and amended slurry pH was determined using a pH probe (WTW, Germany) and the WEP of slurry was measured at the time of land application after Kleinman et al. (2007). Dry matter (DM) content was determined by drying at 105 °C for 16 h. The TP of the dairy cattle slurry was determined after Byrne (1979). Total potassium (TK), total nitrogen (TN) and TP were carried out colorimetrically using an automatic flow-through unit (Varian Spectra 400 Atomic Absorption instrument). Ammoniacal nitrogen ($NH_4$-N) of slurry and amended slurry was extracted from fresh slurry by shaking 10 g of slurry in 200 ml 0.1 M HCl on a peripheral shaker for 1 h and filtering through No 2 Whatman filter paper.

2.3. Slurry amendment and runoff set-up

The results of a laboratory micro-scale study by Brennan et al. (2011) were used to select chemical amendments to be examined in the present study. In addition to a grassed soil-only treatment, five treatments were examined: (i) slurry-only (the study control), (ii) industrial grade liquid alum ($Al_2(SO_4)_3.nH_2O$), comprising 8% aluminium oxide ($Al_2O_3$) applied at a rate of 1.11:1 (Al:TP) (iii) industrial grade liquid poly-aluminium chloride hydroxide (PAC) ($Al_n(OH)_mCl_{3n-m}$) comprising 10% $Al_2O_3$ at a rate of 0.93:1 (Al:TP) (iv) analytical grade $FeCl_2$ at a rate of 2:1 (Fe:TP), and (v) burnt lime ($Ca(OH)_2$) at a rate of 10:1 (Ca:TP). The rates used were based on the results Brennan et al. (2011).

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

$$\frac{C_e}{x/m} = \frac{1}{ab} + \frac{C_e}{b} \qquad (1)$$

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

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

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

where S' is the mass of P adsorbed from slurry (mg $kg^{-1}$), C is the final P concentration of the solution, $k_d$ is the slope of the relationship between S' and C, and $S_0$ is the amount of P originally sorbed to the amendment (mg $L^{-1}$). A slurry sample (from the same storage tank as used in the surface runoff experiments) with a DM of 6%, TP of 550 mg $L^{-1}$ and WEP of 2.26 g $kg^{-1}$ was used for the isotherm study. An approximate metal: soluble P ratio for each amendment was calculated using the *b* term from the Langmuir isotherm and WEP of the slurry. These ratios were equivalent to stoichiometric metal: TP ratios of 0.6:1 compared to 1.1:1 used in the present study for alum and 1.5:1 compared to 0.93:1 for PAC and were generally in agreement with the findings of Brennan et al. (2011), but were not in agreement for $FeCl_2$ (0.4:1 compared to 2:1) and lime (0.9:1 compared to 10:1). The isotherm results indicated that lower application rates should be sufficient to bind P in slurry. However, as the Brennan et al. (2011) study was considered to best replicate surface runoff, it was decided to base the application rates on the results of Brennan et al. (2011) and not the batch test used to develop the Langmuir isotherm. As one of the main aims of the present study was to investigate the effect of amendments on metal release, it was considered to be reasonable and conservative to use results from Brennan et al. (2011). In the case of alum and PAC the rates used were approximately equal to 1:1 metal to TP which was in agreement with Brennan et al (2011) and previous batch studies (Dao and Daniel, 2002). In the case of $FeCl_2$ the most efficient rate used in the Brennan et al (2011) study was examined. When lime applied at 1:1 in Brennan et al (2011) study there was no effect; therefore the results of Brennan et al (2011) study were used. As one of the main aims of the present study was to investigate the effect of amendments on metal release, it was considered to be reasonable and conservative to use results from Brennan et al. (2011).

A laboratory runoff box study was chosen over a field study as it was less expensive and allowed testing under standardized conditions. Such studies are a widely used tool in P transport research to compare treatments (Hart et al., 2004). This experiment used two laboratory runoff boxes, 200-cm-long by 22.5-cm-wide by 5-cm-deep with side walls 2.5 cm higher than the soil surface, and 0.5-cm-diameter drainage holes located at 30-cm-centres in the base (after Regan et al., 2010). Cheese cloth was placed at the base of each runoff box before placing the sods to prevent soil loss. Intact grassed sods 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 sample collection and tests were conducted in triplicate (n=3). Immediately prior to the start of each runoff box experiment, new sods were trimmed and placed in the runoff box; each slab was butted against its adjacent slab to form a continuous surface. Molten candle wax was used to seal any gaps between the soil and the sides of the runoff box, while the joint between adjacent soil samples did not require molten wax.

The packed sods were then saturated using a rotating disc, variable-intensity rainfall simulator (after Williams et al., 1997), comprising a single 1/4HH-SS14SQW nozzle (Spraying Systems Co., Wheaton, IL) attached to a 450-cm-high metal frame, and calibrated to achieve an intensity of 1.15±1 cm $h^{-1}$ and a droplet impact energy of 26 kJ $cm^{-1}$ $ha^{-1}$ at 85% uniformity. The sods were then left to drain for 24 h before the experiment commenced; the grassed sods were then assumed to be at an approximate ‘field capacity’ (Regan et al., 2010). Amendments were added to the slurry and mixed rapidly (10 min at 100 rpm) using a jar test flocculator immediately prior to land application. Slurry and amended slurry were applied directly to the surface of the intact grassed soil in runoff boxes at a rate equivalent to 33 $m^3$ slurry $ha^{-1}$ (26 kg TP $ha^{-1}$), the rate most commonly used in Ireland (Coulter and Lalor, 2008). During each rainfall simulation event, rain was applied until runoff water flowed continuously and then for 1 h while runoff water samples were collected. The drainage holes on the base of the runoff boxes were sealed to better replicate field conditions and to ensure that overland flow occurred. The first rainfall simulation (RS1) commenced 48 h after slurry application, then after a 1 h interval the second rainfall simulation (RS2) commenced. The drainage holes at the bottom of the runoff box were opened for a 24 h interval and then closed when the third rainfall event (RS3) commenced. As the soil samples were taken from the mid-slope of a field with a slope of approximately 5%, it would have been unrealistic to allow the soil to remain water-logged for 24 h between RS2 and RS3. All of the surface runoff was collected at 5-min intervals once runoff began. The source for the water used in the rainfall simulations had a DRP concentration of less than 0.005 mg $L^{-1}$, a pH of 7.7±0.2 and an electrical conductivity (EC) of 0.435 dS $m^{-1}$. Runoff water pH and EC were measured immediately prior to each event using a pH and EC meter.

### 2.4. Sample handling and analysis

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

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

## 2.5. Statistical analysis

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

# 3. Results

## 3.1. Slurry and amended slurry analysis

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

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

## 3.2. Water quality analysis

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

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

The average concentrations of P in runoff water for the 3 rainfall simulation events were 171 μg DRP $L^{-1}$, 91 μg DUP $L^{-1}$ and 373 μg TP $L^{-1}$ for grassed soil-only treatment compared to 655 μg DRP $L^{-1}$, 1,290 μg DUP $L^{-1}$ and 8,390 μg TP $L^{-1}$ for the slurry-control. Incidental DRP and TP concentrations in runoff water following land application of dairy cattle slurry were 5 and 14 times greater than those from grassed-soil. In the present study, alum ($p$<0.001), PAC ($p$<0.001), lime ($p$<0.05) and $FeCl_2$ ($p$<0.05) reduced DRP losses significantly compared to the slurry-control with reductions similar to those observed in the Brennan et al. (2011) study. The results of both studies are tabulated in Table 2. The average FWMC of TDP was significantly reduced compared to the slurry-control. The difference between grass-only, alum and PAC treatments was not significant and the difference between lime and $FeCl_2$ was also not significant. The average FWMC of DUP was also significantly reduced for all treatments compared to slurry-control.

There was no significant difference between TP in runoff water from grass-only (373 μg $L^{-1}$) and alum treatments (506 μg $L^{-1}$). However, there was a significant difference between grass-only and PAC (1,150 μg $L^{-1}$) ($p$< 0.001), lime (1,270 μg $L^{-1}$) and $FeCl_2$ (2,400 μg $L^{-1}$) treatments for TP ($p$< 0.001), with a less significant difference between grass-only and PAC (790 μg $L^{-1}$) and Fe (1,730 μg $L^{-1}$) for PP ($p$< 0.001). Therefore, alum was the best amendment at reducing TP and

PP loss to runoff. Table 2 shows the TP lost in the runoff expressed as a percentage of the slurry applied. The TP losses from control were in agreement with Preedy et al. (2001), who reported that between 6 and 8% of TP applied was lost to runoff. The TP in runoff from the grass-only treatment comprised approximately 47% DRP compared to 69% reported by Haygarth et al. (1998). This difference may be a result of scale effects or differences in experiment design. While chemical amendment of dairy slurry significantly reduced DRP, DUP, PP and TP in runoff water, the proportions of each faction in runoff from alum, PAC and $FeCl_2$ treatments were similar to slurry-control (Fig. 4).

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

### 3.3. Metals in runoff water

The average FWMC of Al, Ca and Fe for the 3 rainfall simulation events are shown in Figs. 6, 7 and 8. The average concentrations of metals tested in runoff water for the 3 rainfall simulation events were greater for the slurry-control than the grass-only treatment. Aluminium to 108 mg Ca $L^{-1}$ ($p<0.01$), and Fe increased from 71 to 151 μg Fe $L^{-1}$ ($p=0.02$, RS2).

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

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

## 4. Discussion

### 4.1. Slurry and amended slurry analysis

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

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

The amendments also changed the pH of the slurry. Lime addition increased slurry pH significantly, resulting in a 25 and 30% reduction in $NH_4$-N and TN of slurry following amendment and mixing (Table 1). This was similar to findings of a study by Molloy and Tunney (1983), who reported an increase in pH to 7.8 and a 50% increase in ammonia ($NH_3$) loss when $CaCl_2$ was added to dairy slurry. This loss in $NH_4$-N was most likely due to $NH_3$ volatilisation, as depending on the pH of a solution, $NH_4$-N can occur as $NH_3$ gas or the ammonium ion ($NH_4$) (Gay and Knowlton, 2005). This reduces the fertiliser value of the slurry and increases $NH_3$ emissions from slurry. Addition of alum, PAC and $FeCl_2$ to dairy cattle slurry significantly reduced pH, as expected. This phenomenon has been reported by a number of studies examining the use of amendments to reduce $NH_3$ losses from dairy cattle slurry (Meisinger et al., 2001; Shi et al., 2001). Meisinger et al. (2001) reported a 60% reduction in $NH_3$ loss from dairy cattle slurry when 2.5% by weight of alum was added in a laboratory batch experiment. In a field study, Shi et al. (2001) reported a 92% reduction in $NH_3$ loss. Moore and Edwards (2005) have shown that chemical amendment improves yields due to increased N efficiency. Future work must examine the impact of amendments on gaseous emissions and the risk of 'pollution swapping' (the increase in one pollutant as a result of a measure introduced to reduce a different pollutant) (Stevens and Quinton, 2008), which must be considered when evaluating amendments for possible recommendations to legislators.

## 4.2. Water quality

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

This study validated the results of a micro-scale study (Brennan et al., 2011) at meso-scale and demonstrated that PAC is the most effective chemical amendment to reduce incidental DRP losses, with alum being most effective at reducing DUP, PP, TP and SS losses arising from land application of dairy cattle slurry. A limited number of runoff studies have been carried out with chemical amendment of dairy cattle slurry (Elliot et al, 2005; Torbert et al., 2005) and swine slurry (Smith et al., 2001b). Torbert et al. (2005) amended landspread composted dairy manure with ferrous sulphate, gypsum and lime (each at 3:1 metal-to-TP ratio) immediately prior to a 40-min rainfall event with overland flow equivalent to a rainfall intensity of 12.4 cm $h^{-1}$. Ferrous sulphate reduced DRP loss by 66.3%, while gypsum and lime amendments increased DRP loss. Lime and gypsum were effective for a short time at the beginning of the event and the authors recommended that lime could be used in areas with infrequent and low volume runoff events. In the Torbert et al. (2005) study, amendments were surface applied to slurry immediately after slurry application and just before the first rainfall simulation event occurred. The differences between the results are likely due to a combination of the shorter contact time with lime before the first rainfall event and less mixing due to different amendment application methods used in each study. In a plot study, Smith et al. (2001b) amended swine manure with alum and $AlCl_3$ at two stoichiometric ratios (0.5:1 and 1:1 Al: TP). Dissolved reactive phosphorus reductions for alum and $AlCl_3$ at the lower ratio were 33 and 45%, respectively, with 84% for both amendments at the higher ratio, which was similar to reductions observed in the current study.

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

In order to minimise the effect of the larger variation in the study control than in runoff from grass-only and amended slurry runoff boxes and to detect differences between treatments, the slurry-control was excluded from the statistical analysis of TP and PP. The reduction in TP and PP losses when alum, PAC and $FeCl_2$ was added to slurry was a result of a combination of precipitation and floc formation, which led to a decrease in SS loss in runoff water. In the case of lime addition, the reductions were a result of the formation of Ca-P precipitates. The average FWMC of TP for the slurry-control during the three rainfall simulation events was 8,390 μg $L^{-1}$. This was similar to 7,000 μg $L^{-1}$ reported by Preedy et al. (2001) in a rainfall simulation study to examine incidental P loss from dairy slurry.

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

### 4.3. Metals in runoff water

Previous studies (Moore et al., 1998; Edwards et al., 1999) have reported that chemical amendment of poultry litter posed no significant risk of increased metal release to runoff water. The findings of the present study also validate this for chemical amendment of dairy cattle slurry. Moore et al. (1998) associated an increase in Ca release from alum treatment to a displacement of Ca in Ca-P bonds by Al. This is also likely to be the cause for PAC and $FeCl_2$ with Ca displaced by Al and Fe. The increase in Ca from the lime treatment was expected as a high rate of lime was applied. The FWMC of Fe (Fig. 8) decreased for all treatments except alum, which increased Fe loss by 30% compared to the slurry-control; this was most likely a result of pH effect of alum, which increased the Fe solubility leading to higher Fe losses. There are acute (acute concentrations being short-term concentration and chronic being a long-term concentration) MAC (750 $\mu g\ L^{-1}$) and chronic MAC (87 $\mu g\ L^{-1}$) for Al in runoff (USEPA, 2009). The Al concentrations observed in the present study were below all MAC with the exception of slurry-control during RS2 and grass-only treatment in RS2, which exceeded chronic MAC. There is no MAC for Ca in water. Iron concentrations in runoff were all below the chronic MAC of 1,000 $\mu g\ L^{-1}$ (USEPA, 2009).

From previous studies, adverse effects are not expected due to alum amendment to manure. In a plot study, Moore el al. (1998) amended poultry litter with alum to examine the effect of alum amendment on runoff concentrations of metals. Alum treatment significantly reduced Fe in runoff. Runoff Al concentrations were not affected by treatment and Ca concentrations increased after treatment. Moore et al. (2000) also found Al loss from a small-scale catchment was unaffected by alum treatment. In order to determine the effect of long-term additions of alum to poultry litter, Moore and Edwards (2005) began a 20-yr study in 1995. The most significant findings of this study were that long-term land application of alum-amended poultry litter did not acidify soil in the same way as $NH_4$-N fertilisers and that Al availability was lower from plots receiving alum-treated poultry manure than $NH_4$-N fertiliser. McFarland et al. (2003) incorporated alum into soil prior to application of dairy dirty water and reported no difference in Al concentrations in runoff between control and alum amended plots.

## 5. Conclusion

The results of this study demonstrate that chemical amendment was very successful in reducing incidental losses of DRP, TP, PP, TDP, DUP and SS from land-applied slurry. The results of the study demonstrate that PAC was the most effective amendment for decreasing DRP losses in runoff following slurry application, while alum was the most effective for TP and PP reduction. Incidental loss of metals (Al, Ca and Fe) from chemically amended dairy cattle slurry was below the MAC for receiving waters. Future research must examine the long-term effect of amendments on P loss to runoff, gaseous emissions, plant availability of P and metal build-up in the soil. If amendments to slurry are to be recommended and adopted as a method to prevent P losses in runoff, the impact of such applications on slurry-borne pathogens, as well as pathogen translocation to the soil and release in surface runoff, needs to be addressed. The long-term effects on microbial communities in soil must also be examined. The results of this study show that even with chemical amendment, P concentration in runoff was above the MAC. Therefore, amendments may not be the best option for minimising incidental P losses, as timing of applications may be just as effective at controlling incidental P losses, and may be much more cost effective. However, chemical amendment immobilises soluble P in slurry and has the potential to reduce chronic P losses. The use of chemical amendments in combination with other mitigation methods such as grass buffer strips would likely increase the effectiveness of the measures. Future work should focus on using amendments to reduce P solubility in slurry to decrease P loss from high P soils by binding P in slurry once it is incorporated into the soil, thereby allowing farmers to apply slurry to soil without further increasing the potential for P loss.


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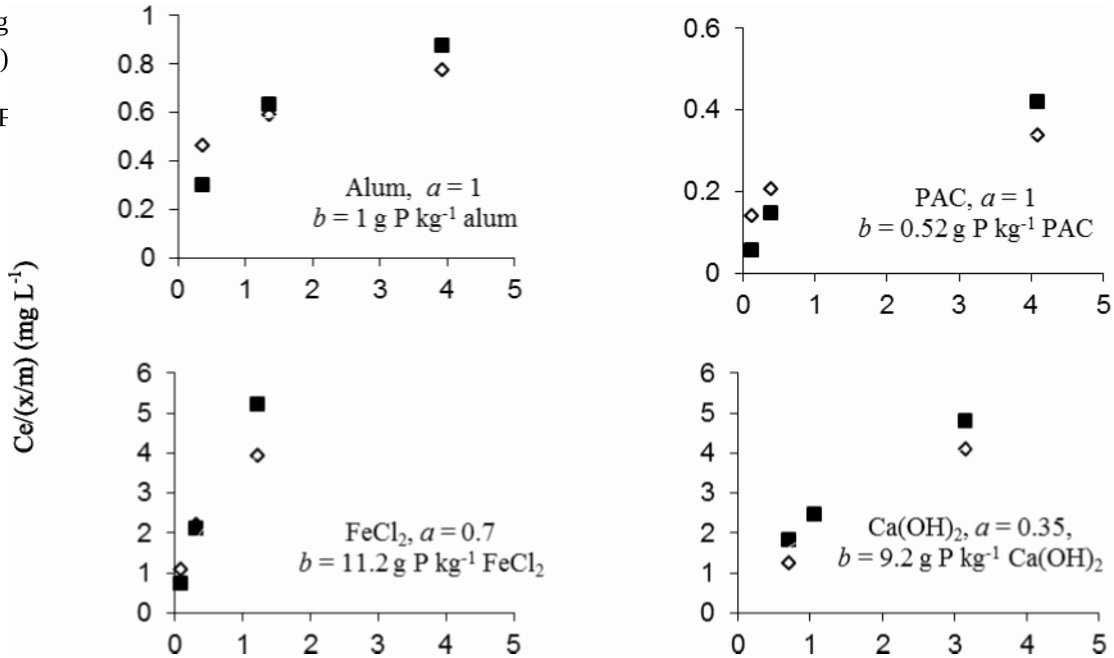
Fig. 6 Average flow weighted mean concentrations of Al in runoff and rain water.

Fig. 7 Average flow weighted mean concentrations of Ca in runoff and rain.

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

Ce (mg L$^{-1}$)

F



Ce/(x/m) (mg L$^{-1}$)
Alum, $a$ = 1
$b$ = 1 g P kg$^{-1}$ alum
PAC, $a$ = 1
$b$ = 0.52 g P kg$^{-1}$ PAC
$FeCl_2$, $a$ = 0.7
$b$ = 11.2 g P kg$^{-1}$ $FeCl_2$
$Ca(OH)_2$, $a$ = 0.35,
$b$ = 9.2 g P kg$^{-1}$ $Ca(OH)_2$

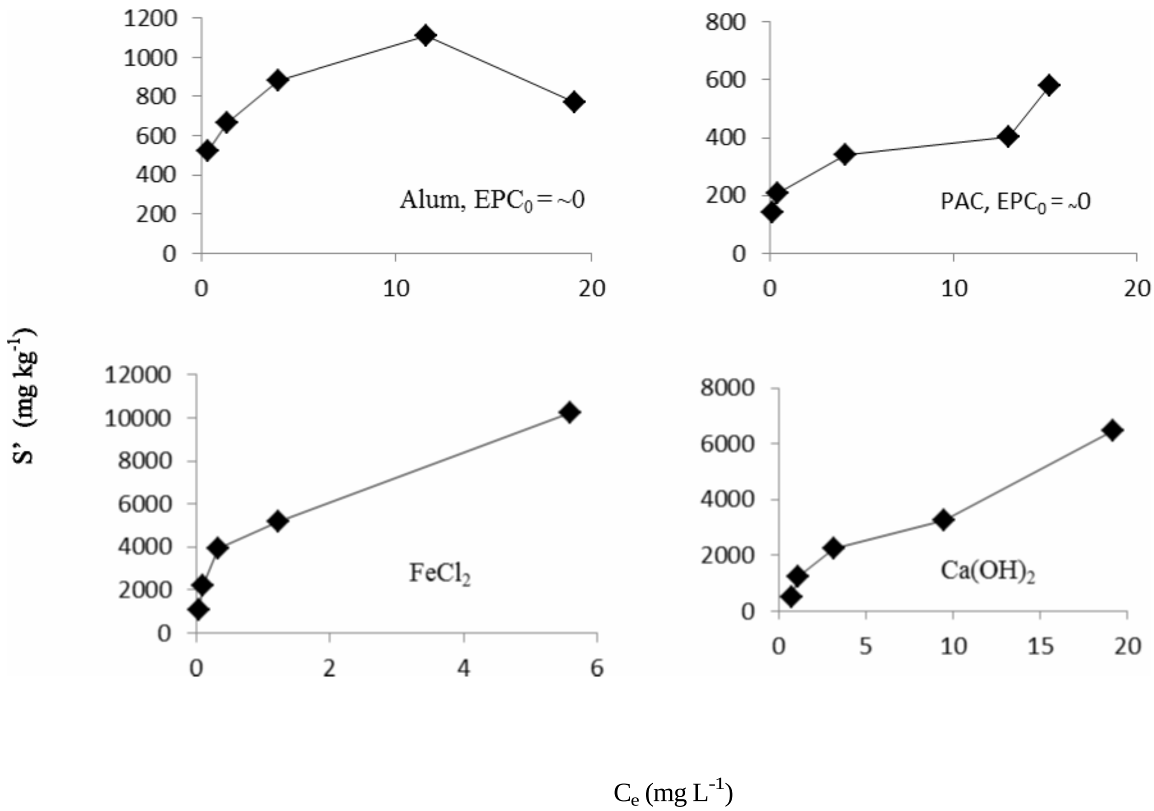



Fig 2 Phosphorus sorption isotherm for amended slurry data.

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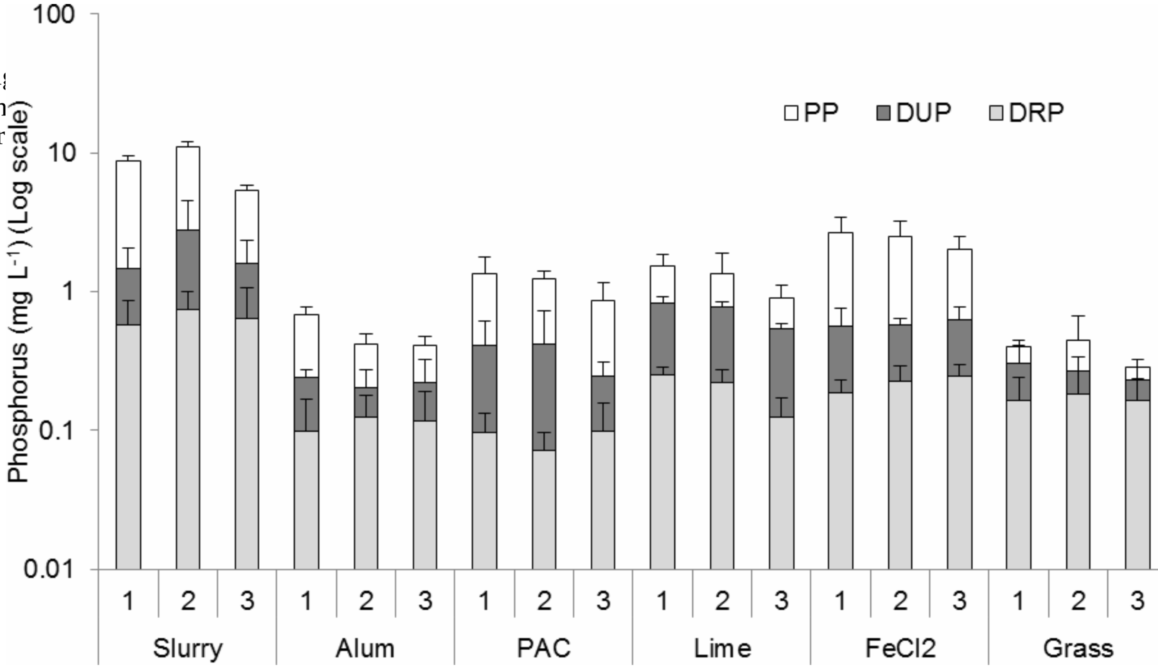

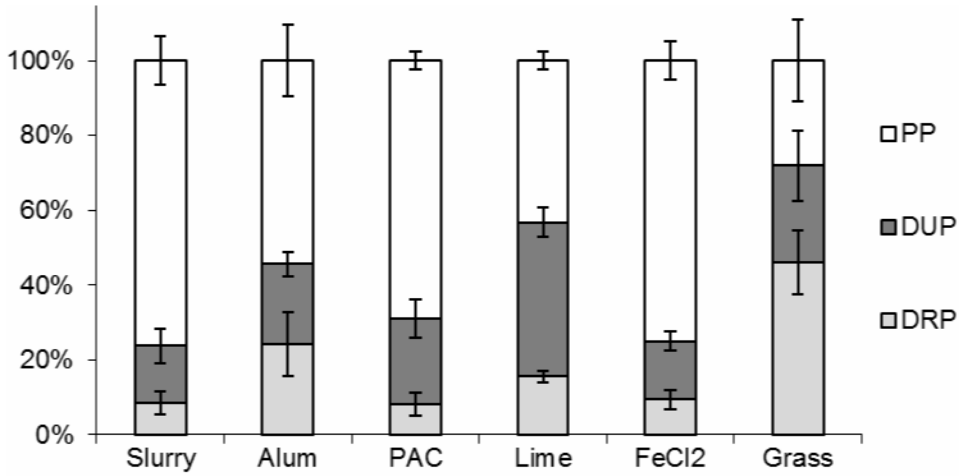


Fig 4 The average % of dissolved reactive phosphorus (DRP), dissolved un reactive phosphorus (DUP) and particulate phosphorus (PP), which comprise total phosphorus (TP) in runoff after three rainfall simulation events.

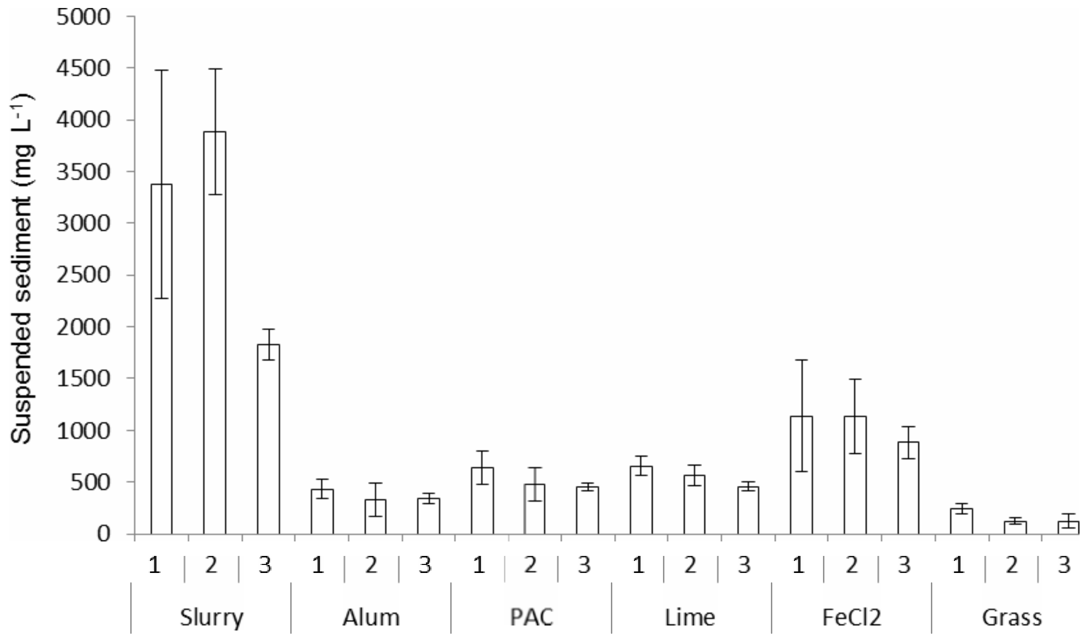


Fig 5 Average flow weighted mean concentrations of suspended sediment in runoff.

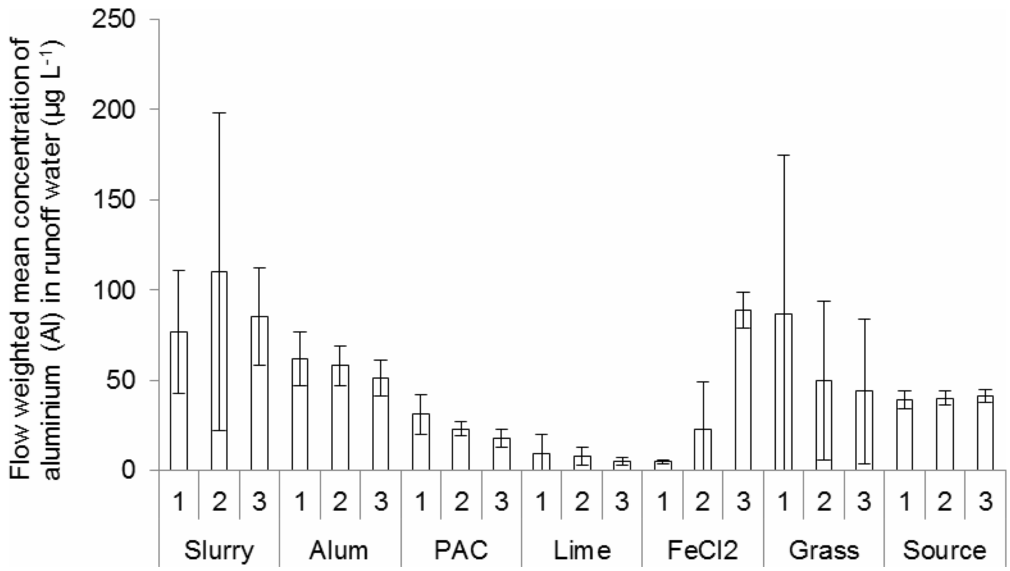


Fig 6 Average flow weighted mean concentrations of Al in runoff and rain water.

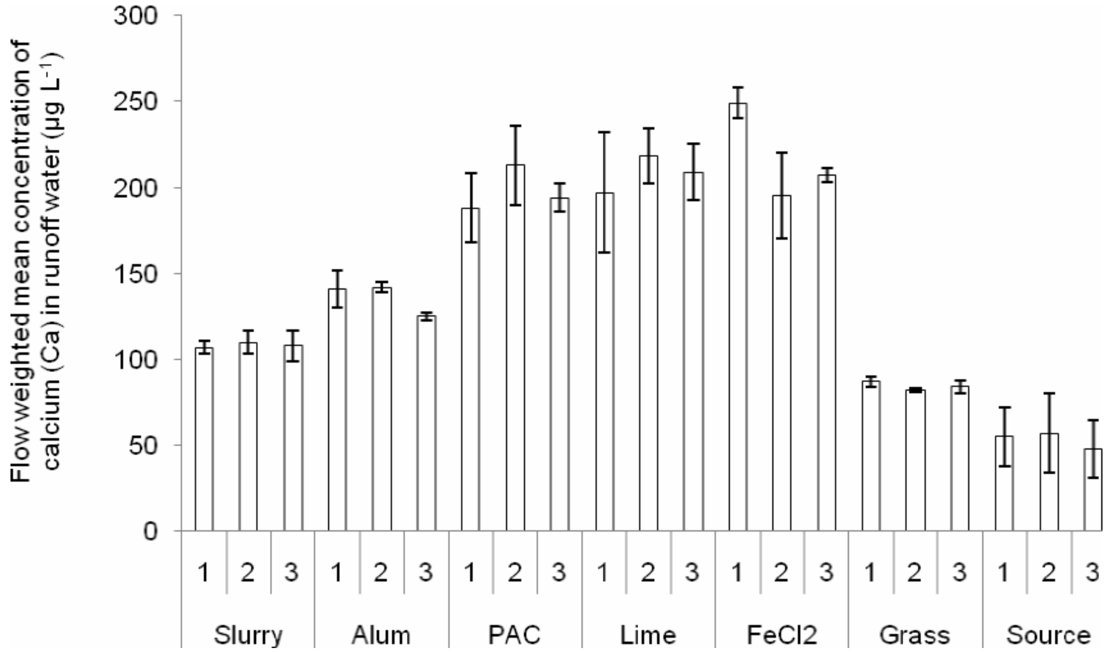


Fig 7 Average flow weighted mean concentrations of Ca in runoff and rain water.

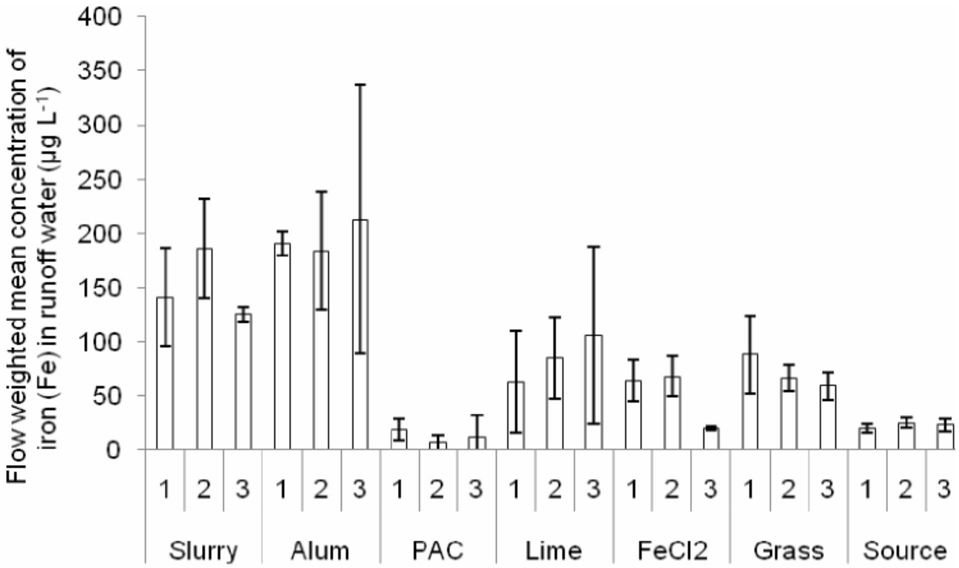


Fig 8 Average flow weighted mean concentrations of Fe in runoff and rain water.

Table 1
Stoichiometric ratio at which the amendments were applied and slurry dry matter (DM), pH and average concentrations of $NH_4$- N, water extractable phosphorus (WEP), total nitrogen (TN), total phosphorus (TP) and total potassium (TK) (n=3).

| | Rate | DM % | pH | $NH_4$-N mg $L^{-1}$ | WEP g $kg^{-1}$ DM | TN mg $L^{-1}$ | TP mg $L^{-1}$ | TK mg $L^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Slurry | | 10.5 (0.04) | 7.47 (0.05) | 1760 (123) | 2.22 (0.34) | 4430 (271) | 1140 (76) | 4480 (218) |
| Alum | 1.1:1 [Al:TP] | 9.4 (0.16) | 5.40 (0.12) | 1770 (21) | 0.002 (0.0004) | 4570 (176) | 1140 (69) | 4360 (84) |
| PAC | 0.93 [Al:TP] | 9.6 (0.28) | 6.37 (0.05) | 1760 (143) | 0.0013 (0.0003) | 4750 (448) | 1180 (165) | 4680 (448) |
| Lime | 10:1 [Ca:TP] | 8.2 (0.29) | 12.2 (0.12) | 1320 (141) | 0.0056 (0.0003) | 3190 (263) | 1140 (96) | 4810 (227) |
| $FeCl_2$ | 2:1 [Fe:TP] | 10.1 (0.22) | 6.7 (0.06) | 1700 (11) | 0.0022 (0.0006) | 4340 (372) | 1120 (51) | 4720 (386) |

() standard deviation

Table 2

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

| Treatment | Preliminary agitator test[a] | | Runoff box | | | | | |
|---|---|---|---|---|---|---|---|---|
| | stoichiometric ratio | DRP reduction | stoichiometric ratio | DRP reduction | Cost per $m^3$ treated slurry[b] | TP loss as % of TP applied | Cost per kg P reduction | P lost per hectare |
| | metal: TP | % | metal: TP | % | € $m^{-3}$ | | € kg $P^{-1}$ | kg P $ha^{-1}$ |
| Slurry | - | - | - | - | 1.90 | 7.70 | - | 2.90 |
| Alum | 0.98:1 | 87 | 1.11:1 | 83 | 7.40 | 0.46 | 66.70 | 0.17 |
| PAC ($AlCl_3$)[c] | 0.98:1 | 88 | 0.93:1 | 86 | 8.80 | 1.05 | 91.10 | 0.40 |
| Lime | 5:1 | 74 | 10:1 | 69 | 10.20 | 1.16 | 111.00 | 0.44 |
| $FeCl_2$ | 2:1 | 88 | 2:1 | 67 | 7.00 | 2.20 | 61.00 | 0.19 |

[a]Taken from Brennan et al. (2011).

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

[c]Laboratory grade aluminium chloride ($Al_2(SO_4)_3.nH_2O$) was used in Brennan et al. (2011). Commercially available commercial grade liquid poly-aluminium chloride was used in the present study.

Note: All treatments were found to be significantly different to the control ($p<0.001$) in the Brennan et al. (2011) study. However, these were not significantly different to each other. In this study, all treatments were significantly different to the slurry-control. Alum and $AlCl_2$ were significantly different to lime and $FeCl_2$, but not to each other. (€1.00 is approximately equal to $1.37or £1.59)