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## **Chemical amendment of pig slurry: control of runoff related risks due to episodic rainfall events up to 48 hours after application**

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### **Abstract**

Losses of phosphorus (P) from soil and slurry during episodic rainfall events can contribute to eutrophication of surface water. However, chemical amendments have the potential to decrease P and suspended solids (SS) losses from land application of slurry. Current legislation attempts to avoid losses to a waterbody by prohibiting slurry spreading when

heavy rainfall is forecast within 48h. Therefore, in some climatic regions slurry spreading opportunities may be limited. The current study examined the impact of three time intervals (TIs) (12, 24 and 48h) between pig slurry application and simulated rainfall with an intensity of  $11.0 \pm 0.59 \text{ mm h}^{-1}$ . Intact grassed soil samples, 1 m long, 0.225 m wide and 0.05 m deep, were placed in runoff boxes and pig slurry or amended pig slurry was applied to the soil surface. The amendments examined were: (1) commercial grade liquid alum (8%  $\text{Al}_2\text{O}_3$ ) applied at a rate of 0.88:1 [Al: total phosphorus (TP)] (2) commercial-grade liquid ferric chloride (38%  $\text{FeCl}_3$ ) applied at a rate of 0.89:1 [Fe:TP] and (3) commercial-grade liquid poly-aluminium chloride (PAC) (10 %  $\text{Al}_2\text{O}_3$ ) applied at a rate of 0.72:1 [Al:TP]. Results showed that an increased TI between slurry application and rainfall led to decreased P and SS losses in runoff, confirming that the prohibition of land-spreading slurry if heavy rain is forecast in the next 48h is justified. Averaged over the three TIs, the addition of amendment reduced all types of P losses to concentrations significantly different ( $p < 0.05$ ) to those from unamended slurry, with no significant difference between treatments. Losses from amended slurry with a TI of 12h were less than from unamended slurry with a TI of 48h, indicating that chemical amendment of slurry may be more effective at ameliorating P loss in runoff than current TI-based legislation. Due to the high cost of amendments, their incorporation into existing management practices can only be justified on a targeted basis where inherent soil characteristics deem their usage suitable to receive amended slurry.

**Keywords:** pig slurry, runoff, P sorbing amendments, Nitrates Directive, Water Framework Directive, phosphorus, suspended solids

## **Introduction**

During episodic rainfall events, phosphorus (P) and reactive nitrogen ( $N_r$ ) fluxes from critical (soil) and incidental (e.g. slurry or fertilizer application) sources can contribute to anthropogenic eutrophication of surface water (Preedy et al. 2001; Kleinmann et al. 2006; Wall et al. 2011). European Union (EU) legislation attempts to optimise nutrient use on agricultural land and to avoid losses to water bodies. The Nitrates Directive (OJEC 1991; Monteny 2001) has been ratified into national legislation in Ireland and limits the magnitude, timing and placement of inorganic and organic fertilizer applications (Jordan et al. 2012). Specifically, it stipulates a mandatory closed period for slurry spreading during winter. Slurry application is limited on soils with a high soil test P (e.g. Morgan's  $P > 8 \text{ mg L}^{-1}$ ), thereby restricting the available land for application (Nolan et al. 2012). Additionally, slurry spreading is prohibited when heavy rainfall is forecast within 48h of application. Therefore, slurry spreading opportunities may be limited, especially in wet years or in areas where soil trafficability is limited due to wet or saturated soil conditions.

Even though there is very clear evidence that P losses in runoff are reduced with increasing time interval (TI) between slurry application and the occurrence of a rainfall-runoff event (Daverede et al. 2004; Hart et al. 2004), most studies have investigated the effect of cumulative rainfall events. Only a few studies have looked at the effect of the TI between slurry application and the first rainfall event (Sharpley 1997; Smith et al. 2007; Allen and Mallarino 2008). Moreover, none of these studies assessed a range of TIs shorter than 48h, which is the limit set by Irish and UK regulations. Assessing the risk of runoff at TIs within these 48h is highly relevant, as the occurrence of heavy rain can often not be ruled out in the highly unpredictable North Atlantic climate (McDonald et al. 2007; Creamer et al. 2010). In addition, this would provide evidence that a 48h limit does not unnecessarily restrict the opportunity of farmers to apply slurry. To our best knowledge, there are no studies that

address the validity of adhering to a 48h dry period between application and the first heavy rainfall event, apart from work by Serrenho et al. (2012), who found that adherence to a minimum TI of 48h between application of dairy soiled water and rainfall was prudent to reduce incidental P losses in runoff. Investigating the development of P losses during first rainfall events within 48h after application can shed more light on the validity and effectiveness of this measure.

Measures to effectively control agricultural P transfer from soil to water include chemical amendment of slurry. Alum, aluminium chloride ( $\text{AlCl}_3$ ), lime and ferric chloride ( $\text{FeCl}_3$ ) have been shown to significantly reduce P losses in surface runoff arising from the land application of dairy cattle slurry (Brennan et al. 2011, 2012), dairy soiled water (Serrenho et al. 2012), poultry litter (Moore et al. 1999, 2000) and pig slurry (Dao 1999; Dou et al. 2003; Smith et al. 2001, 2004; O' Flynn et al. 2012a, b). In particular, O' Flynn et al. (2012b) showed that the runoff losses from amended pig slurry 48h after application could be reduced to levels similar to the soil-only treatment. This warrants the effort of assessing the effectiveness of these additives at TIs of less than 48h between application and first rainfall event.

Therefore, the aim of this study was to investigate the effect of TI (12, 24 and 48h) between pig slurry application and first rainfall event on the losses of P and suspended solids (SS) in runoff, and to assess the efficacy of adding chemical amendments in reducing losses at these three TIs.

## **Materials and Methods**

## **Slurry collection and characterisation**

Pig slurry was taken from an integrated pig unit in Teagasc Research Centre, Moorepark, Fermoy, Co. Cork, Ireland in April 2012. The sampling point was a valve on an outflow pipe between two holding tanks, which were sequentially placed after a holding tank under slats on which no bedding materials were used. To ensure a representative sample, this valve was turned on and left to run for a few minutes before taking a sample. The slurry was stored inside a cold-room fridge at 10°C prior to testing. Total P (TP) and total nitrogen (TN) were determined using persulfate digestion. Ammonium-N ( $\text{NH}_4^+$ -N) was determined by adding 50 ml of slurry to 1 L of 0.1M HCl, shaking for 30 min at 200 rpm, filtering through No. 2 Whatman filter paper, and analysing using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Slurry pH was determined using a pH probe (WTW, Germany). Dry matter content was determined by drying at 105°C for 24h. The physical and chemical characteristics of the pig slurry used in this experiment and characteristic values of pig slurry from other farms in Ireland are presented in Table 1.

## **Pig slurry amendment**

Amendments for the present study were chosen based on effectiveness of P sequestration and feasibility criteria (cost and potential for metals release to the environment (Table 2)) as determined by O' Flynn et al. (2012a, b). The amendment rates, which were applied on a stoichiometric basis, were: (1) commercial grade liquid alum (8%  $\text{Al}_2\text{O}_3$ ) applied at a rate of 0.88:1 [Al:TP] (2) commercial-grade liquid ferric chloride (38%  $\text{FeCl}_3$ ) applied at a rate of 0.89:1 [Fe:TP]; and (3) commercial-grade liquid poly-aluminium chloride (PAC) (10 %

Al<sub>2</sub>O<sub>3</sub>) applied at a rate of 0.72:1 [Al:TP]. The compositions of the amendments used are the same as those used in O' Flynn et al. (2012a, b).

### **Soil collection and analysis**

Intact grassed soil samples 1.2 m long, 0.3 m wide, 0.1 m deep (n=45) were collected from permanent grassland, which had not received fertiliser applications for more than 10 yr, in Galway City, Ireland (53°16'N, -9°02'E). Samples were cut out of the ground with a spade and, to avoid cracking, placed carefully on 1.5 m long, 0.5 m wide timber boards. Between collection and use, soil samples were stored externally to prevent drying. Soil samples (n=3), taken from the upper 0.1 m from the same location, were oven dried at 40 °C for 72h, 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. The particle size distribution was determined using a sieving and pipette method (BSI 1990a) and the organic content of the soil was determined using the loss on ignition test (BSI 1990b). The soil used was a well-drained, sandy loam textured, acid brown earth (WRB classification: Cambisol) (58% sand, 29% silt, 14% clay) with a soil test P of 2.8±0.5 mg L<sup>-1</sup>, making it a P index 1 soil according to The European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2010 (hereafter referred to as S.I. No. 610 of 2010); total potassium (TK) of 203 mg L<sup>-1</sup>, a pH of 6.4±0.3 and an organic matter content of 5±2%.

### **Rainfall simulation study**

The following treatments were examined within 21 d of sample collection: (1) a grassed sod-only treatment with no slurry applied (2) a grassed sod with unamended slurry (the slurry control) applied at a rate of 19 kg TP ha<sup>-1</sup>, and (3) grassed sods receiving amended slurry applied at a rate of 19 kg TP ha<sup>-1</sup>. Three replications of each treatment were subject to rainfall at a TI between application and rainfall of either 12 (TI 1), 24 (TI 2) or 48h (TI 3).

Stainless steel laboratory runoff boxes, constructed by a steel fabricator, 1 m long, 0.225 m wide and 0.075 m deep, with side-walls 0.025 m higher than the grassed sods, were used in this experiment. The runoff boxes were positioned under a rainfall simulator. 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 11.0±0.59 mm h<sup>-1</sup> and a droplet impact energy of 260 kJ mm<sup>-1</sup> ha<sup>-1</sup> at 85% uniformity after Regan et al. (2010). The source for the water used in the rainfall simulations had a dissolved reactive P (DRP) concentration of less than 0.005 mg L<sup>-1</sup>, a pH of 7.7±0.2 and an electrical conductivity of 0.44 dS m<sup>-1</sup>. Each runoff box had 5 mm diameter drainage holes, spaced at distances of 0.3 m centre to centre, positioned in a line and spanning the length of the base, after Regan et al. (2010). Muslin cloth was placed at the base of each runoff box before packing the sods to prevent soil loss. Immediately prior to the start of each experiment, the sods were trimmed and packed in the runoff boxes. To prevent cracking, sods were first trimmed into two 0.5 m lengths and then placed in the runoff box. Each sod was then butted against its adjacent sod 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 joints 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), and left to drain for 24h by opening the 5 mm diameter drainage holes before continuing with the experiment. At this point, when the soil



was at approximately field capacity, slurry and amended slurry were spread on the packed sods and the drainage holes were sealed. They remained sealed for the duration of the experiment. At  $t = 12, 24$  or  $48\text{h}$ , the sods were subjected to a rainfall event, and each event lasted for a duration of 30 min after runoff began. Different sods were used for each rainfall event. Surface runoff samples were collected in 5 min intervals over the 30 min period and in the time period subsequent to the when the rainfall simulator was turned off, until no further runoff samples were available.

Runoff water samples were tested for pH. A subsample was passed through a  $0.45\ \mu\text{m}$  filter and analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Filtered (passed through a  $0.45\ \mu\text{m}$  filter) and unfiltered subsamples, collected at 10, 20 and 30 min after runoff began and any subsequent runoff once rainfall ceased, underwent acid persulfate digestion and were analysed colorimetrically for total dissolved P (TDP) and TP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Particulate phosphorus (PP) was calculated by subtracting TDP from TP. Dissolved un-reactive P was calculated by subtracting DRP from TDP. Suspended solids were tested by vacuum filtration of a well-mixed (previously unfiltered) subsample through Whatman GF/C (pore size:  $1.2\ \mu\text{m}$ ) filter paper. Prior to filtration, the filter paper was weighed. After filtration, the filter paper was dried at  $105^{\circ}\text{C}$  for 24h and reweighed.

### **Statistical analysis**

The data was analysed in R (version 2.15.1, 32 bit) and IBM SPSS 20 using analysis of variance implemented via a general linear model. There were five levels of treatment (soil-only, slurry-only (the study control), and slurry treated with alum, PAC and  $\text{FeCl}_3$ ) and three

levels of the time factor (12, 24 and 48h). Diagnostic plots indicated that a logarithmic transformation of the response variable was desirable when analysing the effects of the predictor variables on the flow weighted mean concentrations (FWMCs; calculated by dividing the total load over a rainfall event by the total flow) of DRP, dissolved un-reactive P, TDP, PP and TP, if the normal distributional assumptions of the analysis were to be met. No transformation was performed for the analysis of SS. Probability values of  $p > 0.05$  were deemed not to be significant.

## **Results**

### **Phosphorus in runoff**

The FWMC of P in runoff from the soil-only treatment showed no statistically significant differences between TIs, with average TP and TDP FWMCs of 0.35 and 0.21 mg L<sup>-1</sup> (corresponding to loads of 2.48 and 1.49 mg m<sup>-2</sup>), respectively (Fig. 1, Table 2). At all TIs, P losses of all forms increased significantly ( $p < 0.05$ ) with slurry application compared with the soil only treatment (Fig. 1). The increase in losses was particularly high for PP, and averaged over the three TIs, the PP in runoff from the soil-only contributed 40% of the TP (Table 2) compared to 67% of the runoff from slurry-only. For the slurry-only treatment, losses of P in runoff significantly ( $p < 0.05$ ) decreased with increasing TI between application and rainfall. The FWMC of TP and TDP decreased from 8.2 and 3.4 mg L<sup>-1</sup> (corresponding to loads of 45.7 and 18.9 mg m<sup>-2</sup>), respectively, at TI 1 to 3.6 and 1.1 mg L<sup>-1</sup> (23.5 and 7.5 mg m<sup>-2</sup>) at TI 3 (Fig. 1).

In general, the addition of chemical amendment significantly ( $p < 0.05$ ) reduced concentrations of all forms of P lost in runoff at each TI to below the lowest losses from slurry-only, i.e. at a TI of 48h (Fig. 1). However, with the exception of DRP, all forms of P losses in runoff from amended slurry were significantly ( $p < 0.05$ ) different to those from soil-only (Table 2). There were generally no significant differences between amendments for P losses in runoff. Time interval had no significant effect on P losses from amended slurry. There was no evidence of any significant interaction between time and treatment type.

### **Suspended solids and pH in runoff**

Losses of SS in runoff from soil-only did not change significantly with TI, with FWMCs of 15.5, 16.9 and 15.6 mg L<sup>-1</sup> (corresponding to loads of 134, 116 and 118 mg m<sup>-2</sup>) after TIs 1, 2 and 3, respectively (Fig. 2). Application of slurry increased SS losses significantly ( $p < 0.001$ ) to levels over 30 times that of soil-only at TI 1 (482 mg L<sup>-1</sup> or 2780 mg m<sup>-2</sup>). Similar to the trends observed in P losses for the slurry-only treatment, losses of SS in runoff decreased with increasing TI between slurry application and rainfall, with statistically significant differences ( $p < 0.05$ ) between each TI. Similar to the P observations, losses of SS in runoff from amended slurry at all TIs were less than the lowest losses from unamended slurry at TI 3 ( $p < 0.05$ ). Whilst diagnostic plots were not entirely satisfactory for SS, all results were extremely clear-cut and there can be no doubt concerning the significance, or otherwise, of the results reported. The variable pH proved to be insignificant in all cases.

## **Discussion**

### **Phosphorus in runoff from soil-only**

The soil used in the present study was P deficient (P index 1), which would not normally be expected to pose a danger of P losses to the environment (Schulte et al. 2010) as such a soil requires additional nutrients to build up soil P reserves. Phosphorus concentrations in runoff from the soil only treatment were often above the Irish surface water regulation of 0.035 mg reactive P L<sup>-1</sup> (S.I. No. 272 of 2009), but overall loads were small and therefore any deleterious effects to a greater scale cannot be inferred. In the field, rainfall would typically be less intense, and the soil would have the capacity for vertical drainage. As a result, the experiment replicated a worst-case scenario in terms of potential P loss from this soil. Therefore, while P losses from the runoff boxes may be used to compare the effects of chemical amendments and TI, they are not an accurate measure of P loss concentration or load to a surface waterbody that might be expected at field-scale.

### **Phosphorus in runoff from unamended slurry**

Decreased losses of P in runoff with increasing TI between application and rainfall have also been found in previous research – but at TIs significantly greater than those examined in the present study. In a plot study, Smith et al. (2007) spread pig slurry at 35 kg P ha<sup>-1</sup> and found that at 30 min rainfall events, each with an intensity of 100 mm h<sup>-1</sup>, DRP concentrations in runoff reduced from 8.4 mg DRP L<sup>-1</sup> at a TI of 1 d to 2.6 mg DRP L<sup>-1</sup> at a TI of 29 d. Allen and Mallarino (2008) spread pig slurry in a plot study at varying rates up to 108 kg P ha<sup>-1</sup> and found that during 30 min rainfall events, each with an intensity of 76 mm h<sup>-1</sup>, DRP and TP loads in runoff were 3.8 and 1.6 times lower at a TI of 10-16 d than at a TI of less than 24h. The trend of an initial peak followed by a gradual reduction may be due to the interaction of the applied P and the conversion from soluble to increasingly recalcitrant forms over time

(Edwards and Daniel 1993). The current study indicates that this process already starts within 24h after application, and confirms that the prohibition of the land-spreading of slurry, if heavy rain is forecast in the next 48h (S.I No. 610 of 2010), is justified.

The extra PP lost in runoff from unamended slurry, associated with sediment and organic material in agricultural runoff, may provide a variable, but long-term, source of P in lakes (Sharpley et al. 1992), and as it is generally bound to the minerals (particularly iron (Fe), Al, and calcium (Ca)) and organic compounds contained in soil, it constitutes a long-term P reserve of low bioavailability (Regan et al. 2010).

### **The effect of slurry amendment on P losses**

The addition of amendment resulted in reduced P losses in runoff compared to unamended slurry, with losses reduced at each TI to below the lowest losses from slurry only. There appeared to be little difference in runoff losses of P between the different amendments (Table 2). Higher losses in runoff from amended slurry than soil-only is because chemical amendment of slurry will only reduce the incidental P losses to the environment, but will not reduce chronic (long-term) P losses from the soil. In a field-based study, Smith et al. (2004) found that  $\text{AlCl}_3$ , added at 0.75% of final slurry volume to slurry from pigs on a phytase-amended diet, could reduce runoff DRP by 73%. In another field-based study, Smith et al. (2001) found that alum and  $\text{AlCl}_3$ , added at a stoichiometric ratio of 0.5:1 Al:TP to pig slurry, achieved reductions of 33% and 45%, respectively, in runoff water, and reductions of 84% in runoff water when adding both alum and  $\text{AlCl}_3$  at 1:1 Al:TP.

Investigation of chemical amendment effectiveness on two soils using identical amendments, spreading rate and TI (Table 3) produced varied results due to differing soil characteristics. Both soils were of a similar texture but have different levels of soil organic carbon. Even though the current study was conducted on a P index 1 soil and had a lower chronic TP loss than measured by O' Flynn et al. (2012b), incidental losses from slurry were higher, but not significantly so. Additionally, the effectiveness of the amendments (PAC, in particular) was much lower than reported by O' Flynn et al. (2012b) (Table 3). This may be explained by differences in soil characteristics between the two experiments: the soil used by O' Flynn et al. (2012b) had a higher buffering capacity (i.e. more binding sites to retain added P) than that of the current study, due to differences in soil composition, including pH and organic matter. This reduction in effectiveness may also be the cause for little difference in P losses between the different amendments (Table 2). The effectiveness of slurry amendments is hence soil-specific and should therefore be examined in future studies.

Based on the results from this study, runoff from amended slurry will have reduced P losses regardless of TI between landspreading and the occurrence of rainfall, indicating that chemical amendment may be more effective in reducing P losses than the current TI-based legislation.

### **Suspended solids and pH in runoff**

As is the case with P, the reduction of SS was also related to the flocculating properties of the amendments. As well as removing PP from suspension, they also aid in adhesion of slurry particles, making them less prone to loss in runoff (Brennan et al. 2011). Apart from soil-only, losses of SS in runoff were all well above  $35 \text{ mg L}^{-1}$ , the treatment standard necessary

for discharge to receiving waters (S.I. No 419 of 1994). However, whilst the results from this laboratory study may be used to compare the effects of chemical amendments and TI, they are not intended as a measure of actual losses to surface water bodies at field-scale.

The effect of amendments on slurry pH is a potential barrier to their implementation as it affects P sorbing ability (Penn et al. 2011) and ammonia (NH<sub>3</sub>) emissions from slurry (Lefcourt and Messinger 2001). However, the results from this laboratory experiment, similar to previous studies (Smith et al. 2004; O' Flynn et al. 2012b), showed that there was no effect on the pH of the runoff water due to the use of amendments. However, further investigation would need to be undertaken to confirm that pollution swapping (the increase in one pollutant as a result of a measure introduced to reduce another pollutant (Healy et al. 2012)) does not occur.

### **Targeted use of amendments**

Due to high costs involved (O' Flynn et al. 2012a), use of chemical amendments in slurry for land application can only be justified on a targeted basis, in particular: (1) soils with high mobilisation potential, soil test P and hydrological transfer potential to surface water i.e. a critical source area; and (2) at times when storage capacity becomes the critical factor, i.e. towards the end of the open period when unpredictable weather conditions would normally prohibit slurry spreading. In these cases, the adoption of the use of chemical amendment of slurry as part of a program of measures would be justified. However, chemical amendments should only be used on soils that have been extensively tested for suitability. The difference in removals experienced in the current study and by O' Flynn et al. (2012b) (Table 3) demonstrates the impact that soil type has on the efficacy of chemical amendment of pig

slurry. The future uptake of such a mitigation strategy is dependent on the additional cost being considered a worthwhile expense, based on weather conditions and regulatory constraints at the time. If climatic conditions and legislation results in inadequate periods during which to spread slurry, and exerts pressure on slurry storage facilities, then chemical amendment may be seen as the most cost-effective and feasible option.

## **Conclusions**

The excessively high losses of P in runoff at TIs of less than 48h after slurry application, combined with the strong decrease of P losses within this time frame, confirm that the prohibition of land-spreading slurry if heavy rain is forecast in the next 48h (S.I No. 610 of 2010) is justified. Chemical amendment of pig slurry was effective at decreasing P and SS losses from the slurry. Runoff P losses from amended slurry were lower than from unamended slurry regardless of TI between land application and the occurrence of rainfall, indicating that chemical amendment may be more effective at reducing P losses than current TI-based legislation. The cumulative deposition of slurry over time, coupled with unpredictable weather patterns, increases the need for amendment, as leaching and overland flow are all possible vectors for pollution. The tightening of environmental legislation or the rigorous enforcement of current Water Framework Directive (European Commission, 2000) legislation means that investment in P reduction will become justified. Due to the high cost of amendments, their incorporation into existing management practices can only be justified on a targeted basis, in particular: (1) critical source areas and (2) towards the end of the open period when unpredictable weather conditions would normally prohibit slurry spreading. However, chemical amendments should only be used on soils that are suitable. There is a pervading difficulty in gaining acceptance for new technologies by farmers, and so strategies



such as those suggested by this study may never be implemented at farm-scale. Future work must be carried out on the refinement of spreading lands within critical source areas based on soil suitability to receive amended slurry.

Chemical amendment has also been used for the poultry and dairy industries, but may also have the potential to be used in the treatment of wastes from other agricultural industries and sludge from wastewater treatment. If chemical amendment becomes a more prevalent practice, then the cost of employing it as a mitigation measure may decrease, making it an even more attractive option. Although encouraging, the effectiveness of the amendments examined in this study must be validated at field-scale.

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## References

Allen BL, Mallarino AP (2008) Effect of liquid swine manure rate, incorporation, and timing of rainfall on phosphorus loss with surface runoff. *J Environ Qual* 37:125-137

Brennan RB, Fenton O, Grant J, Healy MG (2011) Impact of chemical amendment of dairy cattle slurry on phosphorus, suspended sediment and metal loss to runoff from a grassland soil. *Sci Total Environ* 409:5111–5118

Brennan RB, Healy MG, Grant J, Ibrahim TG, Fenton O (2012) Incidental phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry. *Sci Total Environ* 441:132–140

British Standards Institution (1990a) Determination of particle size distribution. British standard methods of test for soils for civil engineering purposes. BSI, London. BS 1377-2

British Standards Institution (1990b) Determination by mass-loss on ignition. British standard methods of test for soils for civil engineering purposes. Chemical and electrochemical tests. BSI, London. BS 1377-3

Creamer RE, Brennan F, Fenton O, Healy MG, Lalor STJ, Lanigan GJ, Regan JT, Griffiths BS (2010) Implications of the proposed Soil Framework Directive on agricultural systems in Atlantic Europe – a review. *Soil Use Manage* 26:197–380

Dao TH (1999) Co-amendments to modify phosphorus extractability and nitrogen/phosphorus ration in feedlot manure and composted manure. *J Environ Qual* 28:1114–1121

Daverede IC, Kravchenko AN, Hoeft RG, Nafziger ED, Bullock DG, Warren JJ, Gonzini LC (2004) Phosphorus runoff from incorporated and surface-applied liquid swine manure and phosphorus fertilizer. *J Environ Qual* 33:1535-1544

Dou Z, Zhang GY, Stout WL, Toth JD, Ferguson JD (2003) Efficacy of alum and coal combustion by-products in stabilizing manure phosphorus. *J Environ Qual* 32:1490–1497

Edwards DR, Daniel TC (1993) Drying interval effects on runoff from fescue plots receiving swine manure. *Trans ASAE* 36:1673–1678

European Commission (2000) Council Directive of 22 December 2000 establishing a framework for the community action in the field of water policy (2000/60/EC).

[www.wfdireland.ie](http://www.wfdireland.ie)

Hart MR, Quin BF, Nguyen ML (2004) Phosphorus runoff from agricultural land and direct fertilizer effects. *J Environ Qual* 33:1954-1972

Healy MG, Ibrahim TG, Lanigan GJ, Serrenho AJ, Fenton O (2012) Nitrate removal rate, efficiency and pollution swapping potential of different organic carbon media in laboratory denitrification bioreactors. *Ecol Eng* 40:198-209

Jordan P, Melland AR, Mellander P-E, Shortle G, Wall D (2012) The seasonality of phosphorus transfers from land to water: Implications for trophic impacts and policy evaluation. *Sci Total Environ* 434:101–109

Kleinman PJA, Srinivasan MS, Dell CJ, Schmidt JP, Sharpley AN, Bryant RB (2006) Role of rainfall intensity and hydrology in nutrient transport via surface runoff. *J Environ Qual* 35:1248-1259

Lefcourt AM, Meisinger JJ (2001) Effect of adding alum or zeolite to dairy slurry on ammonia volatilisation and chemical composition. *J Dairy Sci* 84:1814–1821

McCutcheon GA (1997) MSc Thesis. National University of Ireland, Dublin

McDonald S, Murphy T, Holden N (2007) Spatial and temporal issues in the development of a microbial risk assessment for cryptosporidiosis. In: Holden NM, Hochstrasser T, Schulte RPO, Walsh S (ed) *Making science work on the farm. A workshop on decision support systems for Irish agriculture*. Agmet, Dublin, pp 100-104

Monteney GJ (2001) The EU Nitrates Directive: a European approach to combat water pollution from agriculture. *Sci World J* 1:927–935

Moore Jr. PA, Daniel TC, Edwards DR (1999) Reducing phosphorus runoff and improving poultry production with alum. *Poult Sci* 78:692-698

Moore Jr. PA, Daniel TC, Edwards DR (2000) Reducing phosphorus runoff and inhibiting ammonia loss from poultry manure with aluminum sulfate. *J Environ Qual* 29:37-49

Morgan MF (1941) Chemical soil diagnosis by the universal soil testing system. Connecticut agricultural Experimental Station Bulletin 450. New Haven, Connecticut

Nolan T, Troy SM, Gilkinson S, Frost P, Xie S, Zhan X, Harrington C, Healy MG, Lawlor PG (2012) Economic analyses of pig manure treatment options in Ireland. *Bioresour Technol* 105:15-23

O’Bric C (1992) MSc Thesis. National University of Ireland, Dublin

Official Journal of the European Community (1991) Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources

O’ Flynn CJ, Fenton O, Healy MG (2012a) Evaluation of amendments to control phosphorus losses in runoff from pig slurry applications to land. *Clean Soil Air Water* 40:164–170

O’ Flynn CJ, Fenton O, Wilson P, Healy MG (2012b) Impact of pig slurry amendments on phosphorus, suspended sediment and metal losses in laboratory runoff boxes under simulated rainfall. *J Environ Man* 113:78-84

Penn CJ, Bryant RB, Callahan MA, McGrath JM (2011) Use of industrial byproducts to sorb and retain phosphorus. *Commun Soil Sci Plant Anal* 42:633-644

Preedy N, McTiernan KB, Matthews R, Heathwaite L, Haygarth PM (2001) Rapid incidental phosphorus transfers from grassland. *J Environ Qual* 30:2105-2112

Regan JT, Rodgers M, Healy MG, Kirwan L, Fenton O (2010) Determining phosphorus and sediment release rates from five Irish tillage soils. *J Environ Qual* 39:1-8

Schulte RPO, Melland AR, Fenton O, Herlihy M, Richards KG, Jordan P (2010) Modelling soil phosphorus decline: Expectations of Water Frame Work Directive policies. *Environ Sci Policy* 13:472-484

Serrenho A, Fenton O, Murphy PNC, Grant J, Healy MG (2012) Effect of chemical amendments to dairy soiled water and time between application and rainfall on phosphorus and sediment losses in runoff. *Sci Total Environ* 430:1-7

Sharpley AN, Smith SJ, Jones OR, Berg WA, Coleman GA (1992) The transport of bioavailable phosphorus in agricultural runoff. *J Environ Qual* 21:30-35

Sharpley AN (1997) Rainfall frequency and nitrogen and phosphorus runoff from soil amended with poultry litter. *J Environ Qual* 26:1127-1132

S.I. No. 419 of 1994. Environment Protection Agency Act, 1992 (Urban waste water treatment regulations, 1994). Statutory Office, Dublin

S.I. No. 272 of 2009. European Communities Environmental Objectives (Surface Waters) Regulations 2009. Statutory Office, Dublin

S.I. No. 610 of 2010. European Communities (good agricultural practice for protection of waters) regulations 2010, Statutory Office, Dublin.

Smith DR, Moore Jr. PA, Griffis CL, Daniel TC, Edwards DR, Boothe DL (2001) Effects of alum and aluminium chloride on phosphorus runoff from swine manure. *J Environ Qual* 30:992-998

Smith DR, Moore Jr. PA, Maxwell CV, Haggard BE, Daniel TC (2004) Reducing phosphorus runoff from swine manure with dietary phytase and aluminum chloride. *J Environ Qual* 33:1048-1054

Smith DR, Owens PR, Leytem AB, Warnemuende EA (2007) Nutrient losses from manure and fertilizer applications as impacted by time to first runoff event. *Environ Pol* 147:131-137

Wall D, Jordan P, Melland AR, Mellander P-E, Buckley C, Reaney SM, Shortle G (2011) Using the nutrient transfer continuum concept to evaluate the European Union Nitrates Directive National Action Programme. *Environ Sci Policy* 14:664-674

Williams JD, Wilkins DE, McCool DK, Baarstad LL, Klepper BL, Papendick RI (1997) A new rainfall simulator for use in low-energy rainfall areas. *Appl Eng Agric* 14:243-247

## Figure Captions

**Fig. 1** Histogram of flow-weighted mean concentrations ( $\text{mg L}^{-1}$ ) for dissolved reactive phosphorus (DRP), dissolved un-reactive phosphorus (DUP) and particulate phosphorus (PP) in runoff at time intervals of 12, 24, and 48h after land application of pig slurry

**Fig. 2** Histogram of average flow-weighted mean concentration of suspended solids (SS) ( $\text{mg L}^{-1}$ ) in runoff at time intervals of 12, 24, and 48h after land application of pig slurry



Table 1 Physical and chemical characteristics<sup>a</sup> of the pig slurry used in this experiment and characteristic values of pig slurry from other farms in Ireland

| TP                    | TN      | TK      | NH <sub>4</sub> <sup>+</sup> -N | pH          | DM         | Reference                    |
|-----------------------|---------|---------|---------------------------------|-------------|------------|------------------------------|
| (mg L <sup>-1</sup> ) |         |         |                                 |             | (%)        |                              |
| 482±37                | 3850±20 |         | 2250 ±72                        | 7.37 ± 0.07 | 3.22± 0.15 | The present study            |
| 800                   | 4200    |         |                                 |             |            | S.I. No. 610 of 2010         |
| 1630                  | 6621    | 2666    |                                 |             | 5.77       | McCutcheon 1997 <sup>b</sup> |
| 900±7                 | 4600±21 | 2600±10 |                                 |             | 3.2±2.3    | O' Bric 1991 <sup>b</sup>    |

<sup>a</sup>TP, total P; TN, total N; TK, total K; DM, dry matter. <sup>b</sup>Values changed to mg L<sup>-1</sup> assuming densities of 1 kg L<sup>-1</sup>.

1 Table 2 Flow-weighted mean concentrations ( $\text{mg L}^{-1}$ ) averaged over three time intervals, application costs per tonne, metal application rate ( $\text{kg}$   
 2  $\text{ha}^{-1}$ ), and removals (%) for dissolved reactive P (DRP), dissolved un-reactive P (DUP), total dissolved P (TDP), particulate P (PP), total P (TP)  
 3 and suspended solids (SS)

|                   | DRP                | Removal | DUP                | Removal | TDP                | Removal | PP                 | Removal | TP                 | Removal | SS                  | Removal | Costs                 | Metals              |
|-------------------|--------------------|---------|--------------------|---------|--------------------|---------|--------------------|---------|--------------------|---------|---------------------|---------|-----------------------|---------------------|
|                   | $\text{mg L}^{-1}$ | %       | $\text{mg L}^{-1}$ | %       | $\text{mg L}^{-1}$ | %       | $\text{mg L}^{-1}$ | %       | $\text{mg L}^{-1}$ | %       | $\text{mg L}^{-1}$  | %       | € $\text{tonne}^{-1}$ | $\text{kg ha}^{-1}$ |
| Soil Only         | 0.10 <sup>a</sup>  | -       | 0.11 <sup>a</sup>  | -       | 0.21 <sup>a</sup>  | -       | 0.14 <sup>a</sup>  | -       | 0.35 <sup>a</sup>  | -       | 15.98 <sup>a</sup>  | -       | -                     | -                   |
| Slurry Only       | 1.34 <sup>b</sup>  | -       | 0.60 <sup>c</sup>  | -       | 1.94 <sup>c</sup>  | -       | 3.85 <sup>c</sup>  | -       | 5.78 <sup>c</sup>  | -       | 377.60 <sup>c</sup> | -       | -                     | -                   |
| Alum              | 0.21 <sup>a</sup>  | 84      | 0.28 <sup>b</sup>  | 53      | 0.49 <sup>b</sup>  | 74      | 1.78 <sup>b</sup>  | 54      | 2.27 <sup>b</sup>  | 61      | 101.30 <sup>b</sup> | 73      | 150                   | 16.72 <sup>e</sup>  |
| FeCl <sub>3</sub> | 0.21 <sup>a</sup>  | 84      | 0.19 <sup>b</sup>  | 69      | 0.40 <sup>b</sup>  | 80      | 1.48 <sup>b</sup>  | 61      | 1.88 <sup>b</sup>  | 67      | 139.94 <sup>b</sup> | 63      | 250                   | 16.91 <sup>f</sup>  |
| PAC               | 0.22 <sup>a</sup>  | 84      | 0.26 <sup>b</sup>  | 56      | 0.48 <sup>b</sup>  | 75      | 2.01 <sup>b</sup>  | 48      | 2.49 <sup>b</sup>  | 57      | 135.68 <sup>b</sup> | 64      | 280                   | 13.68 <sup>e</sup>  |

<sup>abcd</sup> Means in a column, which do not share a superscript, were significantly different ( $p < 0.05$ ). <sup>e</sup>Spreading rate of Al. <sup>f</sup>Spreading rate of Fe.

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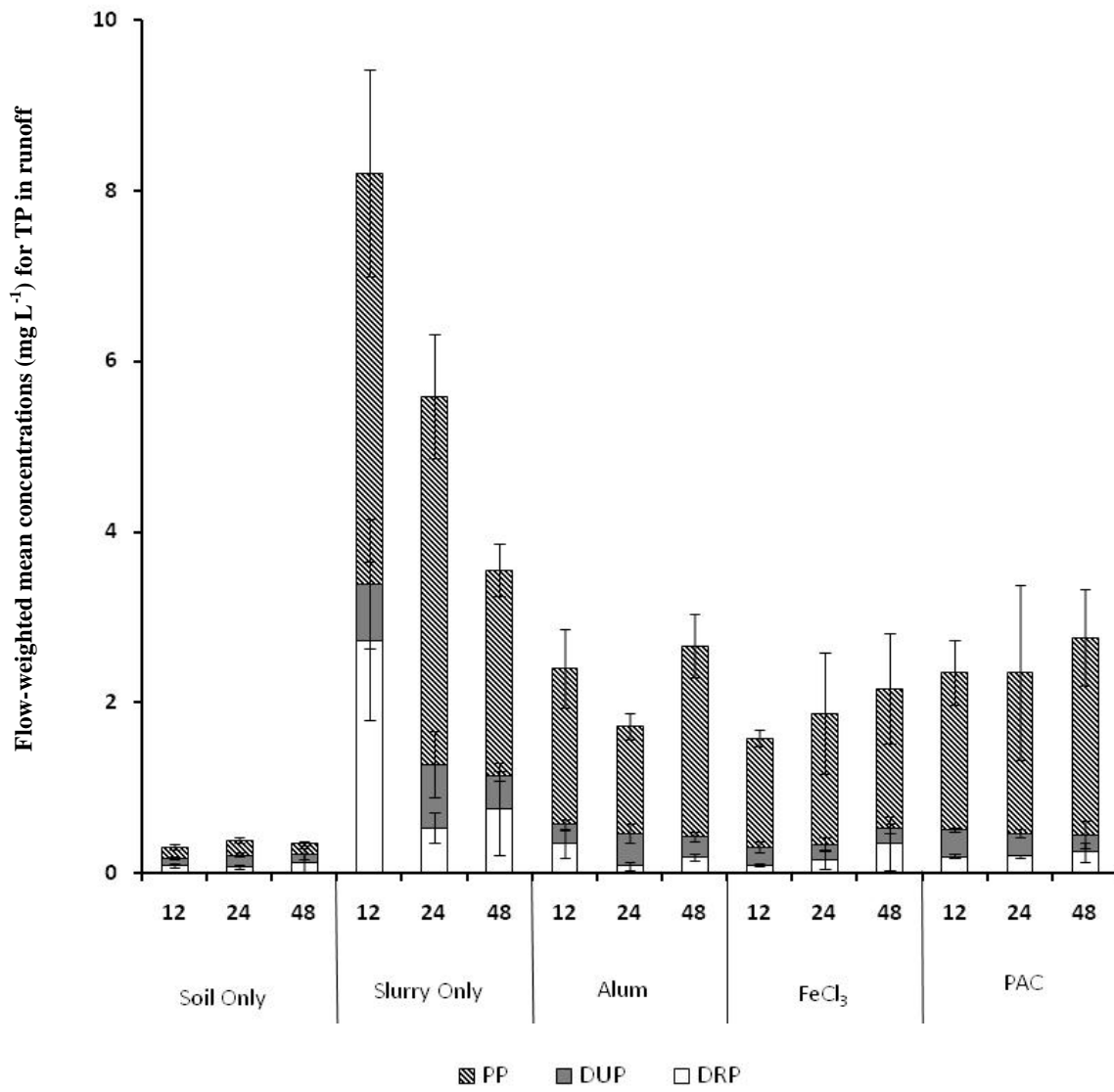
10 Table 3 Comparison of flow-weighted mean concentrations ( $\text{mg L}^{-1}$ ) of total P (TP) in runoff  
 11 from two different soils with identical amendments, spreading rates and time intervals (TIs)<sup>a</sup>

|                                   | Soil 1             |         | Soil 2                  |         |
|-----------------------------------|--------------------|---------|-------------------------|---------|
| Study                             | Current study      |         | O' Flynn et al. (2012b) |         |
| Soil texture                      | Sandy loam         |         | Sandy loam              |         |
| Organic matter (%)                | 5±2                |         | 13±0.1                  |         |
| Soil organic carbon (%)           | 2.8                |         | 7.4                     |         |
| Soil pH                           | 6.4±0.3            |         | 7.65±0.06               |         |
| Parent material                   | Granite            |         | Limestone               |         |
| P index                           | 1                  |         | 4                       |         |
| Morgan's P ( $\text{mg L}^{-1}$ ) | 2.8±0.5            |         | 16.72±3.58              |         |
| Runoff results                    | TP                 | Removal | TP                      | Removal |
|                                   | $\text{mg L}^{-1}$ | (%)     | $\text{mg L}^{-1}$      | (%)     |
| Soil-only                         | 0.36               |         | 0.62                    |         |
| Slurry-only                       | 3.65               |         | 2.68                    |         |
| PAC                               | 2.77               | 24%     | 0.79                    | 71%     |
| Alum                              | 2.08               | 43%     | 1.39                    | 48%     |
| FeCl <sub>3</sub>                 | 2.17               | 41%     | 1.14                    | 57%     |

<sup>a</sup>Runoff results are from rainfall events at TIs of 48h, which occurred in both studies.

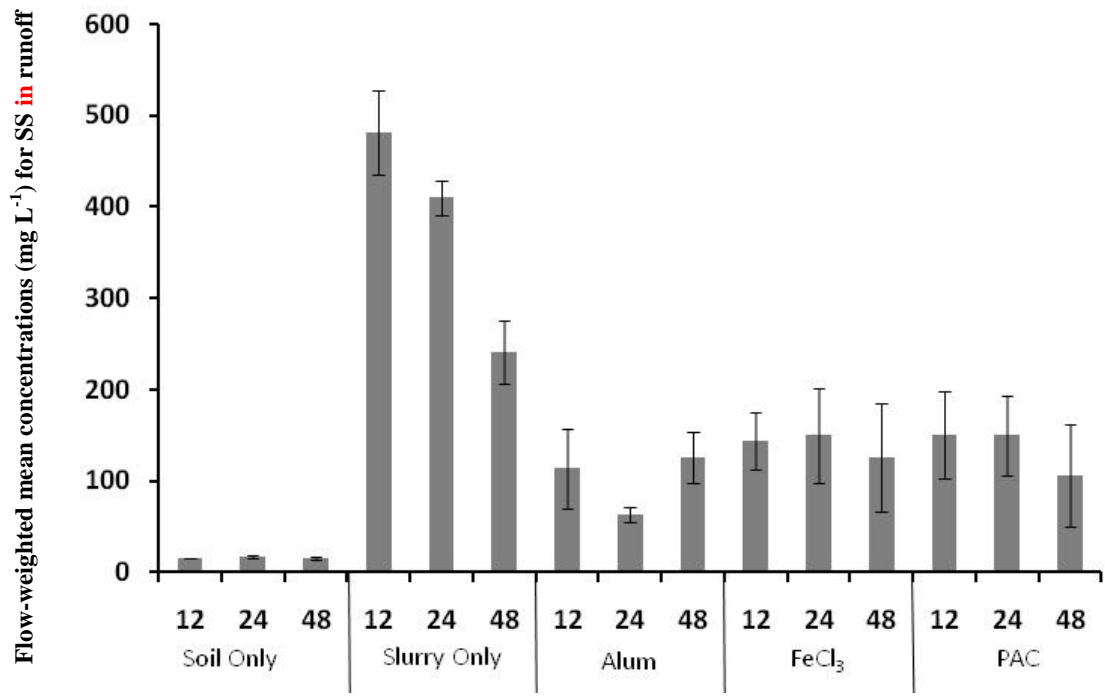
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42 Fig. 1



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58 Fig. 2



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