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Impact of pig slurry amendments on phosphorus, suspended sediment and metal losses in laboratory runoff boxes under simulated rainfall

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Abstract

Losses of phosphorus (P) when pig slurry applications to land are followed by a rainfall event or losses from soils with high P contents can contribute to eutrophication of receiving waters. The addition of amendments to pig slurry spread on high P Index soils may reduce P and suspended sediment (SS) losses. This hypothesis was tested at laboratory-scale using runoff boxes under simulated rainfall conditions. Intact grassed soil samples, 100 cm-long, 22.5 cm-wide and 5 cm-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% Al_2O_3) applied at a rate of 0.88:1 [Al: total phosphorus (TP)] (2) commercial-grade liquid ferric chloride (38% $FeCl_3$) applied at a rate of 0.89:1 [Fe:TP] and (3) commercial-grade liquid poly-aluminium chloride (PAC) (10 % Al_2O_3) applied at a rate of 0.72:1 [Al:TP]. The grassed soil was then subjected to three rainfall events (10.3 ± 0.15 mm h^{-1}) at time intervals of 48, 72, and 96 h following slurry application. Each sod received rainfall on 3 occasions. Results across three rainfall events showed that for the control treatment, the average flow weighted mean concentration (FWMC) of TP was 0.61 mg L^{-1}, of which 31% was particulate phosphorus (PP), and the average FWMC of SS was 38.1 mg L^{-1}. For the slurry treatment, there was an average FWMC of 2.2 mg TP L^{-1}, 47% of which was PP, and the average FWMC of SS was 71.5 mg L^{-1}. Ranked in order of effectiveness from best to worst, PAC reduced the average FWMC of TP to 0.64 mg L^{-1} (42% PP), $FeCl_3$ reduced TP to 0.91 mg L^{-1} (52% PP) and alum reduced TP to 1.08 mg L^{-1} (56% PP). The amendments were in the same order when ranked for effectiveness at reducing SS: PAC (74%), $FeCl_3$ (66%) and alum (39%). Total phosphorus levels in runoff plots receiving amended slurry remained above those from soil only, indicating that, although incidental losses could be mitigated by chemical amendment, chronic losses from the high P index soil in the current study could not be reduced.

Keywords: pig slurry, amendments, runoff, phosphorus, suspended sediment, metals

1. Introduction

The European Union Water Framework Directive (WFD) (European Commission (EC), 2000) aims to achieve 'at least' good ecological status for all water bodies in all member states by 2015 with the implementation of Programmes of Measures (POM) by 2012. Taking Ireland as an example, The European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2010 (hereafter referred to as statutory instrument (S.I.) No. 610 of 2010) is Ireland's POM, which satisfies both the WFD and the Nitrates Directive (European Economic Community (EEC), 1991). The Nitrates Directive promotes the use of good farming practices to protect water quality across Europe by implementing measures to prevent nitrates from agricultural sources polluting a water body. S.I. No. 610 of 2010 imposes a limit on the amount of livestock manure that can be applied to land. As part of this, the maximum amount of livestock manure that may be spread on land, together with manure deposited by the livestock, cannot exceed 170 kg of nitrogen (N) and 49 kg phosphorus (P) ha^{-1} $year^{-1}$. This limit is dependent on grassland stocking rate and soil test P (STP). Presently, these limits may only be exceeded: (1) when spreading spent mushroom compost, poultry manure, or pig slurry (2) if the size of a holding has not increased since 1st August 2006 and (3) if the N application limit is not exceeded (S.I. No. 610 of 2010). The amount by which these limits can be exceeded will be reduced gradually to zero by 1st January, 2017 (Table 1). This will have the effect of reducing the amount of land available for the application of pig slurry and may lead to the need for pig export, which itself becomes energetically questionable at distances over 50 km (Fealy and Schroder, 2008). These new regulations will have an impact on the pig industry, in particular, as it is focused in relatively small areas of Ireland.

At present, pig slurry in Ireland is almost entirely landspread (B. Lynch, pers. comm.). The application of slurry in excess of crop requirements can give rise to elevated STP concentrations, which may take years-to-decades to be reduced to agronomically optimum levels (Schulte et al., 2010). Typically, fields neighbouring farm yards have highest soil P index as they receive preferential organic fertilizer application (Wall et al., 2011). Soil P Index categories of 1 (deficient) to 4 (excessive) are used to classify STP concentrations in Ireland (Schulte et al., 2010). The soil P Index is based on the Morgan's extraction, with a STP of > 8mg L^{-1} classified as P index 4 (S.I. No. 610 of 2010). Soils at soil P Index 4 show no agronomic response to P applications and have a higher risk of P loss in runoff (Tunney, 2000). Phosphorus losses from such a high P Index soil have the potential to become exported along the nutrient transfer continuum within a catchment, and may adversely affect water quality (Wall et al., 2011).

Pig farming in Ireland is concentrated in a small number of counties, with 52% of the national sow herd located in counties Cavan, Cork and Tipperary (Anon, 2008). At 3.5 ha per sow, the density of pig farming in County Cavan is the densest in the country (Anon, 2008). Due to the high concentrations of pig farming in certain areas, the constant application of pig slurry results in the local land becoming high in STP, which leads to an increased long-term danger of P losses (which are known as chronic losses). In addition, due to regulations such as S.I. No. 610 of 2010, the amount of slurry that may be spread on these lands will be reduced, which will lead to a shortage of locally available land on which to spread slurry.

Alternative treatment methods for Irish pig slurry, such as constructed wetlands (CWs), composting and anaerobic digestion (AD), were investigated by Nolan et al. (2012), but landspreading was found to be the most cost effective treatment option. Land being used for other farming practices, such as tillage, which may have a lower STP and would be more suitable for the landspreading of slurry, is still often so far removed from the slurry source as to make transportation of slurry to those locations extremely costly (Nolan et al., 2012).

A possible novel alternative, unexplored by Nolan et al. (2012), is the chemical amendment of pig slurry. Based on a laboratory scale experiment, O'Flynn et al. (2012) suggested that chemical amendment of pig slurry should be explored further, with flow dimensions added, to examine nutrient speciation losses in runoff on a high P Index soil.

Alum, aluminium chloride ($AlCl_3$), lime and ferric chloride are commonly used as coagulants in slurry and wastewater separation operations. Smith et al. (2004) found in a field-based study that $AlCl_3$, added at 0.75% of final slurry volume to slurry from pigs on a phytase-amended diet, could reduce slurry dissolved reactive P (DRP) by 84% and runoff DRP by 73%. In a field study, Smith et al. (2001) found that alum and $AlCl_3$, added at a stoichiometric ratio of 0.5:1 Al: total phosphorus (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 $AlCl_3$ at 1:1 Al:TP. In an incubation study, Dou et al. (2003) found that technical-grade alum, added to pig slurry at 0.25 kg kg^{-1} of slurry dry matter (DM), and flue gas desulpherisation by-product (FGD), added at 0.15 kg kg^{-1}, each reduced DRP by 80%. Dao (1999) amended stockpiled cattle manure with caliche, alum and flyash in an incubation experiment, and reported water extractable P (WEP) reductions in amended manure, compared to the study control, of 21, 60 and 85%, respectively.

O' Flynn et al. (2012) examined the effectiveness and feasibility of six different amendments, added to pig slurry, at reducing DRP concentration in overlying water in an experiment which attempted to simulate a contact mechanism between slurry and soil. Slurry and amended slurry was applied to intact 100-mm-diameter soil cores, positioned in glass beakers. The slurry was left for 24 h and the soil was gently saturated over a further 24 h. 500 mL of water was then added to the beaker. A rectangular paddle, positioned at mid-height in the overlying water, was set to rotate at 20 rpm for 30 h to simulate overland flow, and water samples were taken over the duration of the study and tested for DRP. The effectiveness of the amendments at reducing DRP in overlying water were (in decreasing order): alum (86%), FGD (74 %), poly-aluminium chloride (PAC) (73%), ferric chloride (71 %), flyash (58%) and lime (54%). Ranked in terms of feasibility, which took into account effectiveness, cost and other potential impediments to use, they were: alum, ferric chloride, PAC, flyash, lime and FGD.

However, whilst allowing comparison between different amendments at reducing P in overlying water, the agitator test did not simulate surface runoff of nutrients under conditions which attempted to replicate on-farm scenarios. In the present study, a laboratory runoff box study was chosen over a field study as it was less expensive and conditions such as surface slope, soil conditions, and rainfall intensity can be standardized for testing. The expensive nature of field experiments and inherent variability in natural rainfall has made rainfall simulators a widely used tool in P transport research (Hart et al., 2004). The runoff-box experiment was sufficient to compare treatments and no effort was made to extrapolate field-scale coefficients using this experiment. Unlike previous studies, which used a much higher rainfall intensity of 50 mm h^{-1} (Smith et al., 2001; Smith et al., 2004), the present study examined surface runoff of nutrients under a calibrated rainfall intensity of 10.3±0.15 mm h^{-1}, which has a much shorter return period and is more common in North Western Europe. It is also high enough so as to produce runoff in a reasonable period of time. The present study provides the first comparison of the effects on runoff concentrations and loads following the addition of amendments to Irish pig slurry.

The aim of this laboratory study was to investigate P and suspended sediment (SS) losses during three consecutive simulated rainfall events and to:

1) elucidate if amendment of pig slurry can control incidental (losses which take place when a rainfall event occurs shortly after slurry application and before slurry infiltrates into the soil) and chronic P losses over time to below that of the soil control, and
2) compare how amendment of pig slurry affects P speciation and metal losses in runoff when compared with control and slurry only treatments.

2. Materials and Methods

2.1. Slurry collection and characterisation

Pig slurry was taken from an integrated pig unit in Teagasc Research Centre, Moorepark, Fermoy, Co. Cork in March 2011. The sampling point was a valve on an outflow pipe between two holding tanks, which were sequentially placed after a holding tank under the slats. 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 in a 25-L drum inside a fridge at 4°C prior to testing. The TP and total nitrogen (TN) were determined using persulfate digestion. Ammonium-N (NH_4-N) was determined by adding 50 mL of slurry to 1L 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 (DM) content was determined by drying at 105^{o}C for 24 h. 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 2.

2.2. Soil collection and analysis

120-cm long, 30-cm wide, 10-cm deep intact grassed soil samples (n=15) were collected from a local dry stock farm in Galway, Republic of Ireland. Soil samples (n=3) – taken from the upper 100 mm 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. The particle size distribution was determined using a sieving and pipette method (British Standard (B.S.) 1377-2; BSI, 1990a) and the organic content of the soil was determined using the loss on ignition (LOI) test (B.S.1377-3; BSI, 1990b). The soil used was a poorly-drained, sandy loam textured topsoil (58% sand, 27% silt, 15% clay) with a STP of 16.72±3.58 mg L^{-1} (making it a P index 4 soil according to S.I. No. 610 of 2010, on which P may not be spread, except in those circumstances mentioned in Table 1), total potassium (TK) of 127.39±14.94 mg L^{-1}, a pH of 7.65±0.06 and an organic matter content of 13±0.1%.

2.3. Slurry amendment

The results of a laboratory micro-scale study by O’ Flynn et al. (2012) were used to select amendments and their application rates to be used in the present study. The amendments, which were applied on a stoichiometric basis, were: (1) commercial grade liquid alum (8%

Al_2O_3) applied at a rate of 0.88:1 [Al:TP]; (2) commercial-grade liquid ferric chloride (38% $FeCl_3$) applied at a rate of 0.89:1 [Fe:TP]; and (3) commercial-grade liquid poly-aluminium chloride (PAC) (10 % Al_2O_3) applied at a rate of 0.72:1 [Al:TP]. The other amendments used in the O' Flynn et al. (2012) study (FGD, flyash and lime) were unexamined in the present study on the basis of effectiveness and feasibility. The amendments were added to the slurry in a 2-L plastic container, mixed for 10 s, and then applied evenly to the grassed sods. The compositions of the amendments used are shown in Table 3.

2.4. Rainfall simulation study

100 cm-long, 22.5 cm-wide and 7.5 cm-deep laboratory runoff boxes, with side-walls 2.5 cm 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 10.3±0.15 mm h^{-1} and a droplet impact energy of 260 kJ mm^{-1} ha^{-1} at 85 % uniformity after Regan et al. (2010). 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}. Each runoff box had 5-mm-diameter drainage holes located at 300-mm-centres in 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. The packed sods were then saturated using a rotating disc, variable-intensity rainfall simulator (after Williams et al., 1997), and left to drain for 24 h by opening the 5-mm-diameter drainage holes before continuing with the experiment. At this point (t = 24 h), 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. They were then left for 48 h in accordance with S.I. No. 610 of 2010. At t = 72 h, 96 h and 120 h (Rainfall Event (RE) 1, RE 2 and RE 3), rainfall was applied (to the same sods), and each event lasted for a duration of 30 min after runoff began. Surface runoff samples for each event were collected in 5-min intervals over this 30-min period. The laboratory runoff box experiment was sufficient to compare treatments and no effort was made to extrapolate field-scale coefficients using this experiment.

2.5. Runoff collection and analysis

The following treatments were examined in triplicate (n=3) 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^{-1}, and (3) grassed sods receiving amended slurry applied at a rate of 19 kg TP ha^{-1}.

After each 5-min interval, runoff water samples were tested for pH. A subsample was passed through a 0.45μm filter and analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Filtered (passed through a 0.45μm filter) and unfiltered subsamples, collected at 10, 20 and 30 min after runoff began, were tested for total dissolved phosphorus (TDP) and TP using acid persulfate digestion. Particulate phosphorus was calculated by subtracting TDP from TP. Dissolved un-reactive phosphorus was calculated by subtracting DRP from TDP. Suspended sediment was tested by vacuum filtration of a well-mixed (previously unfiltered) subsample through Whatman GF/C (pore size: 1.2 μm) filter paper. As the amendments used contain metals, namely Al and Fe, filtered subsamples collected at 10, 20 and 30 min after runoff began, were analysed using an

ICP (inductively coupled plasma) VISTA-MPX (Varian, California). The limit of detection was 0.01 mg L^{-1}.

2.6. Statistical analysis

This experiment analysed the pairwise comparisons of the mean concentrations of DRP, DUP, TDP, PP, TP, SS, Al and Fe in the runoff when slurry only (slurry control), no slurry, and slurry that was treated with alum, PAC and $FeCl_3$, was applied. The significances of the pairwise comparisons were based upon the results of an analysis of the data by a multivariate linear model in SPSS 19 (IBM, 2011). Covariance structures and interactions were investigated, but found not to be of significance with respect to the pairwise comparisons. Probability values of $p>0.05$ were deemed not to be significant.

3. Results and Discussion

3.1. Phosphorus in runoff

The vast majority of the Irish landscape has rolling topography and is highly dissected with surface water or drainage systems. The present laboratory experiment mimics a field neighboring such a landscape. The high drainage density, high annual rainfall and low annual potential evapotranspiration (20–50% of rainfall) facilitates the hydrological pathways for transfers of P (Wall et al., 2011). However, the losses from the runoff boxes in the present study may be buffered further before reaching this export continuum.

The flow weighted mean concentrations (FWMC) of P in runoff from the soil-only treatment were constant for all REs, with TP and TDP decreasing from 0.62 and 0.42 mg L^{-1} (corresponding to loads of 3.6 and 2.5 mg m^{-2}), respectively, during RE 1 to 0.60 and 0.41 mg L^{-1} (3.4 and 2.3 mg m^{-2}) during RE 3 (Fig. 1). These concentrations of TP were above 0.03 mg P L^{-1}, the median phosphate level above which significant deterioration in water quality may be seen in rivers (Clabby et al., 2008). These high losses were as expected as the soil used was a P index 4 soil, which carries the risk of increased P loss in runoff (Tunney, 2000) and may not normally have P spread on it (S.I. No. 610 of 2010). Although the buffering capacity of water ensures that the concentration of the water in a stream or lake will not be as high as the concentration of runoff, chronic losses of P are a major issue in water quality.

Phosphorus losses of all types increased with slurry application (Fig. 1). The FWMC of DRP for the runoff from the slurry control, averaged over the three rainfall events, was 0.89 mg L^{-1} (4.47 mg m^{-2}), which was significantly different to, and over twice as high as the soil-only treatment ($p=0.00$) (Table 4). Although the concentration of TDP in runoff from the slurry control decreased slightly during each event (Fig. 1), the TDP fraction of TP increased from 45% during RE1 to 55% during RE2, and 66% during RE3. This was due to the level of PP in runoff reducing, albeit not significantly ($p>0.05$), between each event. A similar trend was replicated across all amended slurry treatments. As PP is generally bound to the minerals (particularly Fe, Al, and Ca) and organic compounds contained in soil, and constitutes a long-term P reserve of low bioavailability (Regan et al., 2010), it may provide a variable, but long-term, source of P in lakes as it is associated with sediment and organic material in agricultural runoff (Sharpley et al., 1992). The average FWMC of 0.89 mg DRP L^{-1} (4.47 mg m^{-2}) from the slurry control was consistent with the results of Smith et al. (2001), who obtained DRP concentrations of 5.5 mg L^{-1} in surface runoff following slurry application to grassland at 44.9 kg TP ha^{-1} and subjected to a rainfall intensity of 50 mm h^{-1}, 1 day after application.

Poly-aluminium chloride was the best performing amendment, and significantly reduced all P to concentrations not significantly different ($p>0.05$) to soil-only. Across all treatments, no form of P changed significantly between REs ($p>0.05$). Within each treatment and each event, there were certain variances between replications expressed as standard deviations from the average. These may be attributable to the inherent variability within soils and slurry, such as differing chemical and physical properties, from two very non-homogeneous materials.

The amendments used in this study all significantly reduced DRP, DUP, TDP, PP and TP concentrations in the runoff water compared to the slurry control, but resulted in DRP concentrations which were not significantly different ($p>0.05$) to the soil-only treatment. No statistical relationship was found between the runoff P concentrations and pH, or volume of runoff water measured during each test. Dissolved un-reactive phosphorus concentrations from all amendments were not significantly different to each other ($p>0.05$) and were significantly higher than the soil-only, but lower than the slurry control. Similarly, the addition of amendments reduced the PP, TP and TDP losses below the slurry control (Table 4); however, they were still higher than the soil-only. This indicates that even after chemical amendment, slurry spread on high STP soil still poses an environmental danger. This is because chemical amendment of slurry will only affect the contribution of the slurry to runoff P, but will not affect the contribution of the soil itself which, for high STP soils, may still pose the danger of chronic P losses.

The average FWMC of DRP and TDP in runoff from the amended slurry treatments were approximately half than in the runoff from the slurry control. This may be due to the amendments reducing the DRP of the slurry itself, similar to what Smith et al. (2001) experienced. Smith et al. (2001) added alum and $AlCl_3$, each at 0.5:1 and 1:1 Al:TP, to pig slurry. Each reduced DRP in pig slurry by roughly 77% at 0.5:1 and 99% at 1:1. At the low rate of application (0.5:1), DRP in runoff water was reduced by 33 and 45% when adding alum and $AlCl_3$, respectively. At the high rate of application (1:1), each amendment reduced runoff DRP by 84%. These were similar to the results obtained from the present study, which ranged from 63% for alum added at 0.88:1 Al:TP to 71% for PAC added at 0.72:1 (Table 4).

3.2. Suspended sediment, metals and pH in runoff

The SS concentration in runoff reduced during each RE, apart from the soil-only treatment, which was more constant. The amendments all reduced the SS concentration to below that of the slurry control (Fig. 2) and, in the case of $FeCl_3$ and PAC, the average FWMC was below 35 mg L^{-1}, the treatment standard necessary for discharge to receiving waters (S.I. No 419 of 1994). However, the concentration of SS in the soil-only treatment and the slurry control were highly variable. The SS concentrations in runoff were not significantly different between treatments, apart from PAC, which was significantly different to the slurry control ($p=0.024$).

The order of effectiveness of removal was the same as for P, i.e. from best to worst, they are: PAC, $FeCl_3$ and alum. The removals of SS for alum (39 %), $FeCl_3$ (66 %) and PAC (74 %) were not as high as those reported by Brennan et al. (2011), who reported SS removals of 88%, 65% and 83% in runoff when adding alum, $FeCl_3$ and PAC, respectively, to dairy cattle slurry. However, the DM of the dairy cattle slurry used by Brennan et al. (2011) was 10.5%, compared to 3.41% in this study, and all treatments resulted in average FWMCs well above the slurry only treatment of the present study.

Figure 3 shows the average FWMCs of Al and Fe in runoff water. As expected, alum and PAC resulted in increased levels of Al, with Al levels in runoff from alum significantly different to all other treatments ($p<0.05$). This agrees with Edwards et al. (1999), who reported increased levels of Al in runoff water from alum-amended horse manure and municipal sludge, compared to the slurry control, in a plot study. Edwards et al. (1999) added alum at 10% by dry manure and dry sludge mass. Horse manure and municipal sludge were spread at 9.3 and 7.8 Mg ha^{-1}, respectively, with rainfall applied within 1 h of application at 64 mm h^{-1} for 30 min after runoff began. The FWMC of Al in runoff increased from 1.22 and 0.61 mg L^{-1} from unamended horse manure and municipal sludge, respectively, to 1.80 and 1.01 mg L^{-1} for alum-amended horse manure and municipal sludge. In the present study, Al from PAC was significantly lower than from alum ($p=0.00$), significantly higher than from $FeCl_3$ ($p=0.036$), but not significantly different to the soil-only or slurry control ($p>0.05$). $FeCl_3$ resulted in increased levels of Fe, significantly different ($p<0.05$) to all other treatments. Alum reduced Fe levels in runoff compared to the slurry control. This result was in agreement with Moore et al. (1998) and Edwards et al. (1999). Moore et al. (1998) added alum at 10% by weight in a plot study to poultry litter, which was spread at varying land application rates up to 8.98 Mg ha^{-1}. Rainfall was applied immediately after slurry application (RE1), and 7 days later (RE2) at 50 mm h^{-1} for 27.5 min after runoff began. At the highest land application rate, Fe loads in runoff were reduced from 94.2 and 31.1 g ha^{-1} from the slurry control for RE1 and RE2 to 37.8 and 12.1 g ha^{-1} from the alum-amended litter. Edwards et al. (1999) reported a FWMC of 0.17 mg Fe L^{-1} in runoff from alum-amended horse manure, compared to 0.44 mg L^{-1} from unamended slurry, and 0.10 from soil-only. There are no limits for levels of Al in surface water intended for the abstraction of drinking water, but the concentrations of Fe measured in the runoff were well within the mandatory limit of 0.3 mg L^{-1}(EEC, 1975).

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_3) emissions from slurry (Lefcourt and Messinger, 2001). The use of acidifying amendments can lead to an increased release of hydrogen sulphide gas (H_2S) from slurry, which is believed to be responsible for human and animal deaths when slurry is agitated on farms. However, the results from this laboratory experiment showed the pH of the runoff water not to be significantly affected by the use of amendments ($p>0.05$). 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.

3.3. Outlook for use of amendments as a mitigation measure

In this laboratory study, amendments to pig slurry significantly reduced runoff P from runoff boxes compared to the slurry control. However, the DRP concentration in runoff remained at or above the DRP concentration in runoff from soil only, indicating that, although incidental losses can be mitigated by chemical amendment, chronic losses cannot be reduced. Future research must examine the effect of amendments on P loss to runoff at field-scale under real-life conditions with conditions which laboratory testing cannot mimic, such as the presence of drainage, flow dynamics and a watertable. Other research which must also be carried out includes the effect of amendments on leachate, gaseous emissions and plant available P.

The use of amendments also incurs the extra cost of purchasing amendments. O' Flynn et al. (2012) estimated that the cost of spreading amended slurry at the stoichiometric rates used in this study would be 3.33, 2.45, and 3.69 € m^{-3} for alum, $FeCl_3$, and PAC, respectively. This would be in comparison to 1.56 € m^{-3} to spread unamended slurry.

Increased regulation of pig slurry management will accentuate the problem of chronic P losses. A possible solution, unexamined in the present study, would be to modify the soil with a P sorbing material.

4. Conclusions

The findings of this study were:

1. On the high soil test phosphorus soil tested, phosphorus losses from the grassed soil only were high and were further increased following slurry application. All amendments tested reduced all types of phosphorus losses, but did not reduce them significantly to below that of the soil-only treatment, the average flow-weighted mean concentration of total phosphorus of which was 0.61 mg L^{-1} and which comprised 31% as particulate phosphorus. For the slurry control, the average flow weighted mean concentration of the surface runoff was 2.17 mg total phosphorus L^{-1}, 47% of which was particulate phosphorus. In decreasing order of effectiveness at removal of phosphorus, the most successful amendments were: commercial-grade liquid poly-aluminium chloride, which reduced the average flow weighted mean concentration of total phosphorus to 0.64 mg L^{-1} (42% particulate phosphorus); commercial-grade liquid ferric chloride, which reduced total phosphorus to 0.91 mg L^{-1} (52% particulate

phosphorus); and alum, which reduced total phosphorus to 1.08 mg L^{-1} (56% particulate phosphorus).

2. For each treatment, total phosphorus and total dissolved phosphorus concentrations in runoff decreased after each rainfall event. However, the fraction of total dissolved phosphorus within runoff increased, due to large, although not significant, decreases in particulate phosphorus between events.
3. The amendments all reduced the suspended sediment to below that of the slurry control, and in the case of commercial-grade liquid ferric chloride and commercial-grade liquid poly-aluminium chloride, to below that of the soil only. These two treatments also reduced the average flow weighted mean concentration of suspended sediment to below 35 mg L^{-1}, the treatment standard necessary for discharge to receiving waters.
4. Although encouraging, the effectiveness of the amendments trialed in this study should be validated at field scale.

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References

Anon, 2008. A development strategy for the Irish pig industry, 2008 to 2015. Teagasc, Rep. of Ireland. http://www.teagasc.ie/pigs/advisory_services/Strategy_group_report_Final_08.pdf (accessed 02/02/2012).

Anon, 2010. Summary of main agreed changes to nitrates regulations. Teagasc, Rep. of Ireland. http://www.teagasc.ie/pigs/advisory_services/NitratesRegsChanges_Oct2010.pdf (accessed 02/02/2012).

Brennan, R.B., Fenton, O., Grant, J., Healy, M.G., 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.

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

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. BS 1377. London: BSI.

Clabby, K.J., Bradley, C., Craig, M., Daly, D., Lucey, J., O’Boyle, S., O’Donnell, C., McDermott, G., McGarrigle, M., Tierney, D., Wilkes, R., Bowman, J., 2008. Water quality in Ireland 2004-2006. EPA, Wexford. http://www.epa.ie/downloads/ pubs/water/waterqua/waterrep/ (accessed 31.01.12).

Dao, T.H., 1999. Co-amendments to modify phosphorus extractability and nitrogen/phosphorus ration in feedlot manure and composted manure. J. Environ. Qual. 28, 1114–1121.

Dou, Z., Zhang, G.Y., Stout, W.L., Toth, J.D., Ferguson J.D., 2003. Efficacy of alum and coal combustion by-products in stabilizing manure phosphorus. J. Environ. Qual. 32, 1490–1497.

EC, 2000. Council Directive of 22 December 2000 establishing a framework for the Community action in the field of water policy (2000/60/EC). http://www.wfdireland.ie/ (accessed 31.01.12).

Edwards D.R., Moore P.A., Workman S.R., Bushee E.L., 1999. Runoff of metals from alum-treated horse manure and municipal sludge. J. Am. Water Resour. Assoc. 35, 155–165.

EEC, 1975. Council Directive of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States (75/440/EEC) http://eur-lex.europa.eu/LexUriServ/site/en/consleg/1975/L/01975L0440-19911223-en.pdf (accessed 31.01.2012).

EEC, 1991. Council Directive of 12 December 1991 concerning the protection of waters against pollution by nitrates from agricultural sources (91/676/EEC) http://www.environ.ie/en/Environment/Water/WaterQuality/NitratesDirective/ (accessed 31.01.2012).

Fealy, R., Schroder, J., 2008. Assessment of manure transport distances and their impact on economic and energy costs. International Fertiliser Society Conference, Cambridge, 12 December, 2008.

Hart, M.R., Quin, B.F., Nguyen M.L., 2004. Phosphorus runoff from agricultural land and direct fertilizer effects. J. Environ. Qual. 33, 1954–1972.

Healy, M.G., Ibrahim, T.G., Lanigan, G.J., Serrenho, A.J., 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.

Lefcourt, A.M., Meisinger, J.J., 2001. Effect of adding alum or zeolite to dairy slurry on ammonia volatilisation and chemical composition. J. Dairy Sci. 84, 1814–1821.

McCutcheon, G.A., 1997. MSc Thesis, National University of Ireland, Dublin.

Moore, P.A., Daniel, T.C., Gilmour, J.T., Shreve, B.R., Edwards, D.R., Wood, B.H., 1998. Decreasing metal runoff from poultry litter with aluminum sulphate. J. Environ. Qual. 27, 92–99.

Morgan, M.F., 1941. Chemical soil diagnosis by the universal soil testing system. Connecticut. Connecticut. New Haven: Connecticut agricultural Experimental Station Bulletin 450.

Nolan, T., Troy, S.M., Gilkinson, S., Frost, P., Xie, S., Zhan, X., Harrington, C., Healy, M.G., Lawlor, P.G., 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 1992.

O' Flynn, C.J., Fenton, O., Healy, M.G., 2012. Evaluation of amendments to control phosphorus losses in runoff from pig slurry applications to land. Clean – Soil, Air, Wat. In press. DOI: 10.1002/clen.201100206

Penn, C.J., Bryant, R.B., Callahan, M.A., McGrath, J.M., 2011. Use of industrial byproducts to sorb and retain phosphorus. Commun. Soil Sci. Plant Anal. 42, 633-644.

Regan, J.T., Rodgers, M., Healy, M.G., Kirwan, L., Fenton, O., 2010. Determining phosphorus and sediment release rates from five Irish tillage soils. J. Environ. Qual. 39, 1-8.

Schulte, R.P.O., Melland, A.R., Fenton, O., Herlihy, M., Richards, K.G., Jordan, P., 2010. Modelling soil phosphorus decline: Expectations of Water Frame Work Directive policies. Environ. Sci. Policy. 13, 472-484.

Sharpley, A.N., Smith, S.J., Jones, O.R., Berg, W.A., Coleman, G.A., 1992. The transport of bioavailable phosphorus in agricultural runoff. J. Environ. Qual. 21, 30-35.

S.I. No. 419 of 1994. Environment Protection Agency Act, 1992 (Urban waste water treatment regulations, 1994). http://www.irishstatutebook.ie/1994/en/si/0419.html (accessed 22.12.2011).

S.I. No. 610 of 2010. European Communities (good agricultural practice for protection of waters) regulations 2010. http://www.environ.ie/en/Legislation/Environment/Water/FileDownLoad,25133,en.pdf. (accessed 22.12.2011).

Smith, D.R., Moore Jr., P.A., Griffis, C.L., Daniel, T.C., Edwards, D.R., Boothe. D.L., 2001. Effects of alum and aluminium chloride on phosphorus runoff from swine manure. J. Environ. Qual. 30, 992-998.

Smith, D.R., Moore Jr., P.A., Maxwell, C.V., Haggard, B.E., Daniel, T.C., 2004. Reducing phosphorus runoff from swine manure with dietary phytase and aluminum chloride. J. Environ. Qual. 33, 1048-1054.

Tunney, H., 2000. Phosphorus needs of grassland soils and loss to water. In: Steenvoorden, J., Claessen, F., Willems, J. (Eds.), Agricultural effects on ground and surface waters: Research at the edge of science and society. IAHS, Wallingford, England, 273, pp. 63–69

Wall, D., Jordan, P., Melland, A.R., Mellander, P.E., Buckley, C., Reaney, S.M., 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, J.D., Wilkins, D.E., McCool, D.K., Baarstad, L.L., Klepper, B.L. Papendick, R.I., 1997. A new rainfall simulator for use in low-energy rainfall areas. Appl. Eng. Agric. 14, 243–247.

Fig. 1. Histogram of flow-weighted mean concentrations (mg L^{-1}) for dissolved reactive phosphorus (DRP), dissolved unreactive phosphorus (DUP) and particulate phosphorus (PP) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry. Hatched line = 30 µg P L^{-1} standard (Clabby et al., 2008).

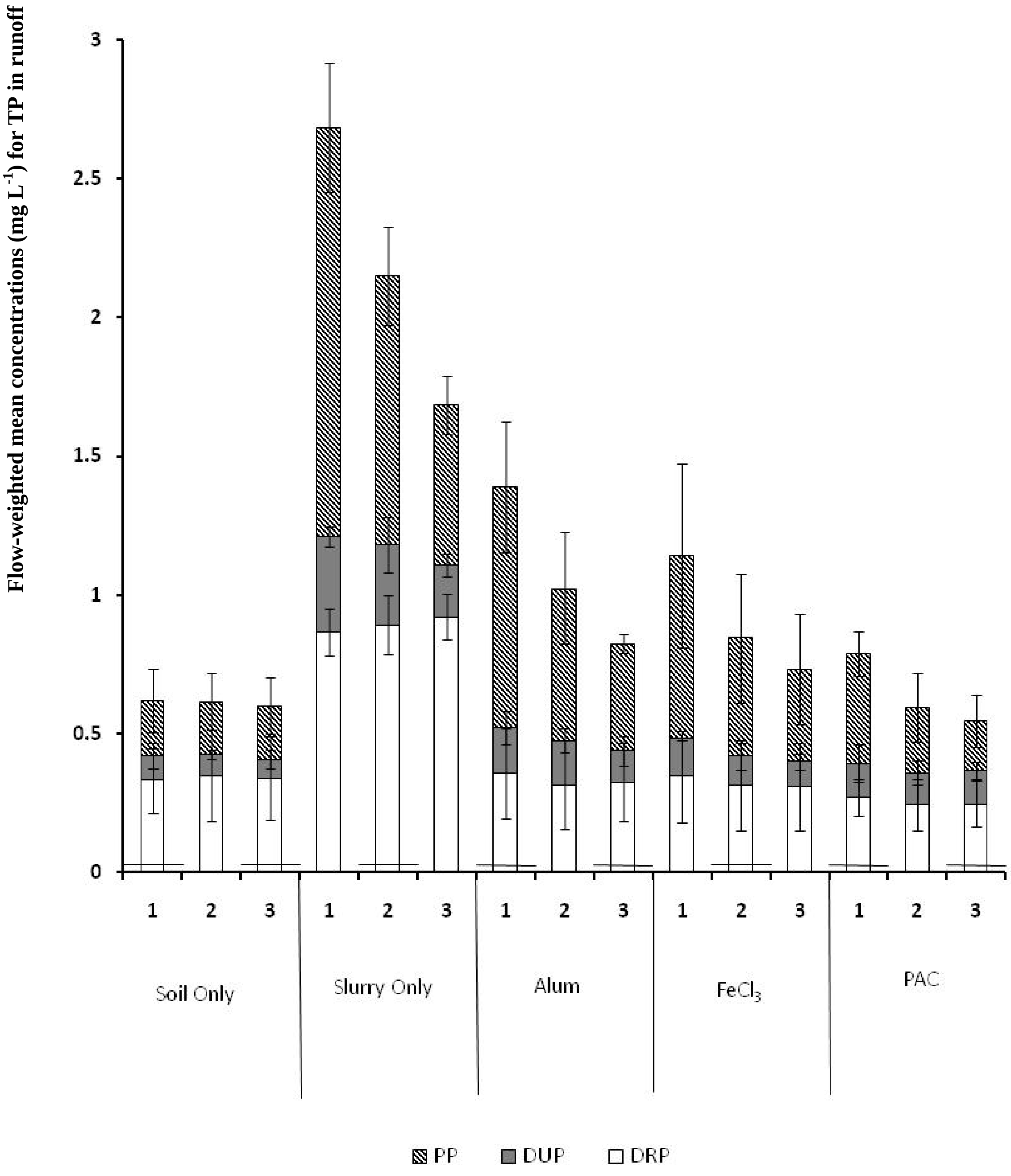

Fig. 2. Histogram of average flow-weighted mean concentration of suspended sediment (SS) (mg L^{-1}) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry. Hatched line = 35 mg L^{-1} standard (S.I. No 419 of 1994).

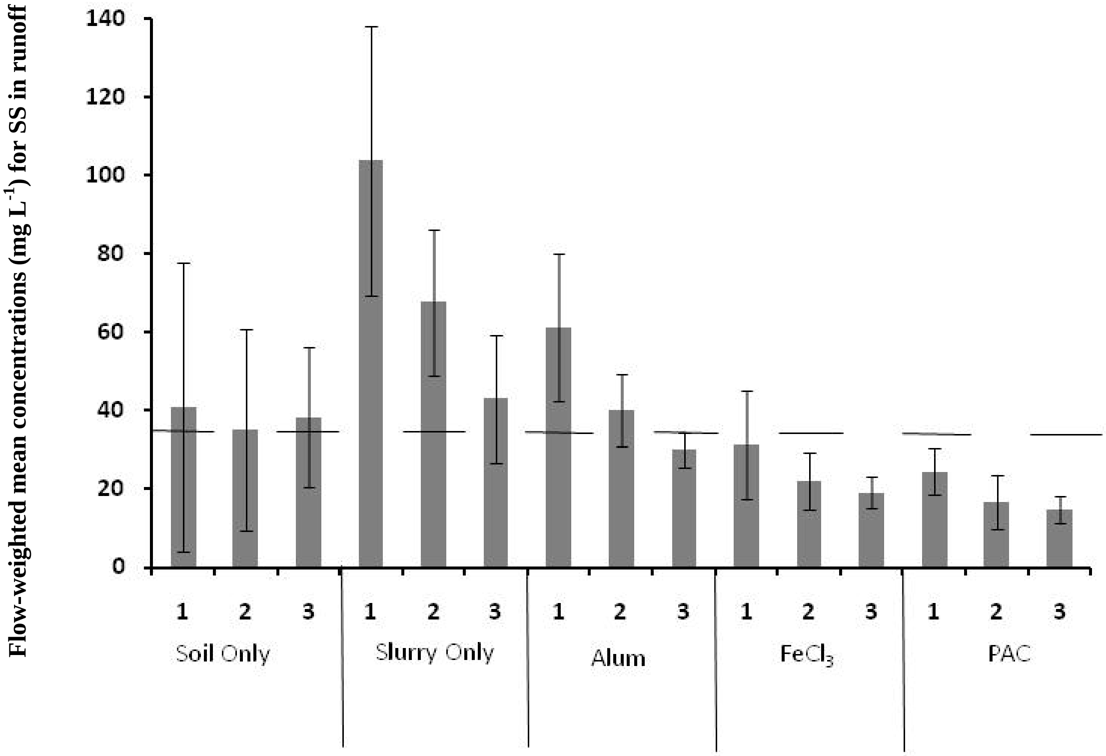

Fig. 3. Histogram of average flow-weighted mean concentration of metals (mg L^{-1}) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry.

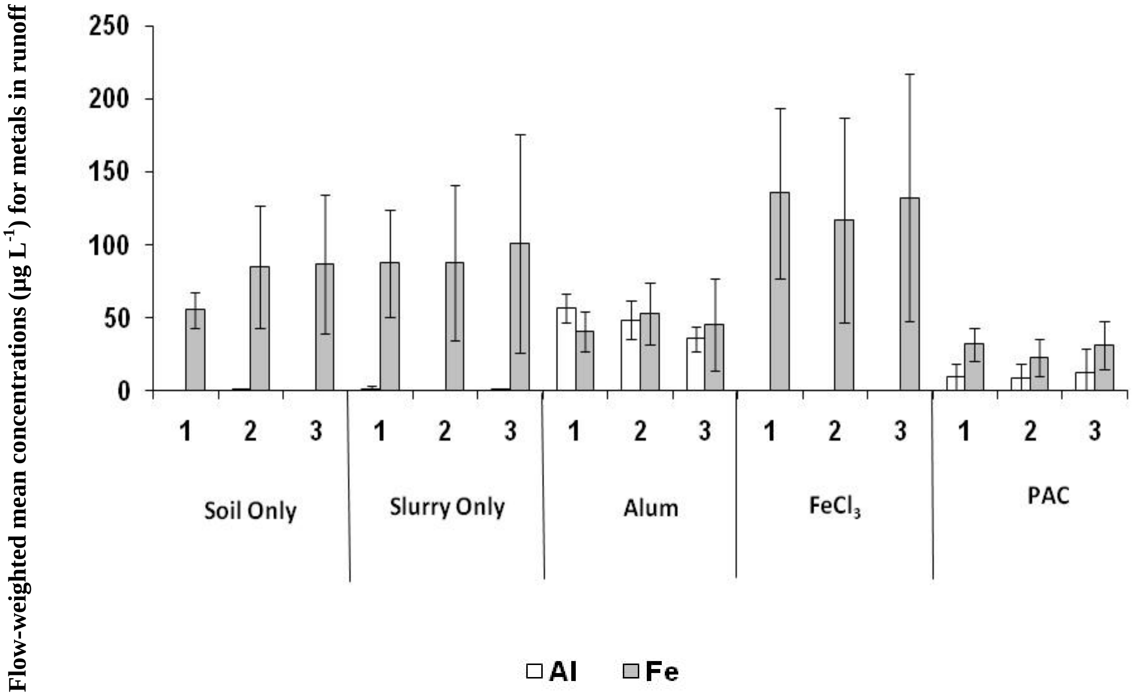

Table 1. Amount by which regulations may be exceeded over time.

Date	Amount by which regulations can be exceeded (kg P ha^{-1})
To January 1, 2013[a]	Not limited
January 1, 2013 - January 1, 2015	5
January 1, 2015 - January 1, 2017	3
January 1, 2017 onwards	0

[a] Up to 1 January 2013, the regulation limits can be exceeded when spreading spent mushroom compost, poultry manure, or pig slurry (Anon 2010, www.teagasc.ie). This can only happen if the activities which produce this on a holding have not increased in scale since 1 August 2006, and the N application limit is not exceeded (S.I. No. 610 of 2010).

Table 2. Physical and chemical characteristics of the pig slurry used in this experiment and characteristic values of pig slurry from other farms in Ireland.

TP	TN	TK	NH_4-N	pH	DM	Reference
(mg L^{-1})					(%)	
613±40	2800±212		2290 ±39	7.85 ± 0.03	3.41± 0.08	The present study
800	4200					S.I. No. 610 of 2010
1630	6621	2666			5.77	McCutcheon, 1997[a]
900±7	4600±21	2600±10			3.2±2.3	O' Bric, 1991[a]

[a] Values changed to mg L^{-1} assuming densities of 1 kg L^{-1}, ± standard deviation

Table 3. Characterisation of amendments used in this study (O’ Flynn et al., 2012)

Amendment		Alum	Ferric Chloride	PAC
		8% Al_2O_3	38% $FeCl_3$	10 % Al_2O_3
pH		1.25		1.0 – 3.0
WEP	mg kg^{-1}	0		
Al	%	4.23		
Ca				
Fe		<0.01	38	
K				
As	mg kg^{-1}	1	<2.8	<1.0
Cd		0.21	<3.4	<0.2
Co				
Cr		2.1	<48	<2.0
Cu			<65	
Mg				
Mn			<1370	
Mo				
Na				
Ni		1.4	<48	<1.0
P				
Pb		2.8	<14	<2.0
V				
Zn				
Sb			<2.8	<1.0
Se			<2.8	<1.0
Hg			<0.7	<0.2

Table 4. Flow-weighted mean concentrations (mg L^{-1}) averaged over three rainfall events, and removals (%) for dissolved reactive P (DRP), dissolved un-reactive P (DUP), total dissolved P (TDP), particulate P (PP), total P (TP), and suspended sediment (SS).

	DRP mg L^{-1}	Removal %	DUP mg L^{-1}	Removal %	TDP mg L^{-1}	Removal %	PP mg L^{-1}	Removal %	TP mg L^{-1}	Removal %	SS mg L^{-1}	Removal %
Soil Only	0.34^{ab}	-	0.08^{a}	-	0.42^{a}	-	0.19^{a}	-	0.61^{a}	-	38.06^{ab}	-
Slurry Only	0.89^{c}	-	0.27^{b}	-	1.17^{b}	-	1.01^{b}	-	2.17^{b}	-	71.52^{b}	-
Alum	0.33^{a}	63	0.15^{c}	46	0.48^{a}	59	0.60^{cd}	40	1.08^{cd}	50	43.82^{ab}	39
$FeCl_3$	0.32^{b}	64	0.11^{c}	59	0.43^{c}	63	0.47^{c}	53	0.91^{c}	58	24.27^{ab}	66
PAC	0.26^{ab}	71	0.12^{c}	56	0.37^{ac}	68	0.27^{ad}	73	0.64^{ad}	70	18.61^{a}	74

[abcd] Means in a column, which do not share a superscript, were significantly different ($P < 0.05$)