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Impact of chemically amended pig slurry on greenhouse gas emissions, soil properties and leachate

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Abstract

The effectiveness of chemical amendment of pig slurry to ameliorate phosphorus (P) losses in runoff is well studied, but research mainly has concentrated only on the runoff pathway. The aims of this study were to investigate changes to leachate nutrient losses, soil properties and greenhouse gas (GHG) emissions due to the chemical amendment of pig slurry spread at 19 kg total phosphorus (TP), 90 kg total nitrogen (TN), and 180 kg total carbon (TC) ha⁻¹. The amendments examined were: (1) commercial grade liquid alum (8% Al₂O₃) applied at a rate of 0.88:1 [Al:TP] (2) commercial-grade liquid ferric chloride (38% FeCl₃) applied at a rate of

0.89:1 [Fe:TP] and (3) commercial-grade liquid poly-aluminium chloride (PAC) (10% Al₂O₃) applied at a rate of 0.72:1 [Al:TP]. Columns filled with sieved soil were incubated for 8 mo at 10°C and were leached with 160 ml (19 mm) distilled water wk⁻¹. All amendments reduced the Morgan's phosphorus and water extractable P content of the soil to that of the soil-only treatment, indicating that they have the ability to reduce P loss in leachate following slurry application. There were no significant differences between treatments for nitrogen (N) or carbon (C) in leachate or soil, indicating no deleterious impact on reactive N emissions or soil C cycling. Chemical amendment posed no significant change to GHG emissions from pig slurry, and in the cases of alum and PAC, reduced cumulative N₂O and CO₂ losses. Chemical amendment of land applied pig slurry can reduce P in runoff without any negative impact on nutrient leaching and GHG emissions. Future work must be conducted to ascertain if more significant reductions in GHG emissions are possible with chemical amendments.

Keywords: pig slurry; P sorbing amendments; Water Framework Directive; nitrate

1. Introduction

The European Union Water Framework Directive (EU WFD) (European Commission (EC), 2000) aims to achieve 'at least' good ecological status for all water bodies, including rivers, lakes, groundwater, estuaries and coastal waters, in all member states by 2015. To meet this objective, Programmes of Measures (POM) must be implemented in all EU member states. In Ireland, POM are enacted by the Nitrates Directive (European Economic Community, 1991), which, amongst other measures, limits the magnitude, timing and placement of inorganic fertilizer and organic manure applications to land.

In Ireland, as part of the National Action Programme (NAP) to address the requirements of the EU WFD, the maximum amount of livestock manure that may be spread on land, together with manure deposited by the livestock, cannot exceed 170 kg nitrogen (N) ha⁻¹ yr⁻¹ and 49 kg phosphorus (P) ha⁻¹ yr⁻¹. This limit is dependent on grassland stocking rate and soil test phosphorus (STP; based on plant available Morgan's P (P_m)). Soil P Index categories of 1 (deficient) to 4 (excessive) are used to classify STP concentrations in Ireland (Schulte et al., 2010). Phosphorus losses from P Index 4 soils have the potential to become exported along the transfer continuum within a catchment, and may adversely affect surface and groundwater quality (Wall et al., 2011). The amount by which these limits can be exceeded will be reduced gradually to zero by January 1, 2017. These new regulations will have an impact on the pig industry in particular, as it is focused in relatively small areas of Ireland, and will, in effect, reduce the amount of land available for the application of pig slurry. This may lead to the need for pig slurry export, which is energetically questionable at distances over 50 km (Fealy and Schroder, 2008).

Landspreading is currently the most cost effective treatment option for pig slurry in Ireland (Nolan et al., 2012). Due to the high concentrations of pig farming in certain areas, in the midlands and south of the country especially, the constant application of pig slurry results in certain fields (those nearest the farm or the most suitable areas for spreading (Wall et al., 2011)) becoming high in STP, which may take years-to-decades to be reduced to agronomically optimum levels (Schulte et al., 2010).

When applications of pig slurry are followed by rainfall events, incidental (short-term), diffuse transfers of P and N may occur in runoff. Losses of both P and N may also occur through leaching, which ultimately could have adverse consequences for water bodies

(McDowell and Sharpley, 2001; Fenton et al., 2011; Sophocleous, 2011). Karstified aquifers, which are overlain by free-draining soils, are particularly susceptible to groundwater pollution, as they have less attenuation potential than surface runoff pathways and there is a high potential for macropore flow of dissolved and particulate forms of P (Kramers et al., 2012). In Ireland, karstified limestone covers approximately 20% of the area of the country (Daly, 2005), and much pig farming is conducted in karst-covered areas.

Chemical amendment of pig slurry has been shown to be an effective means of reducing surface runoff of P and suspended sediment (SS) by numerous researchers (Smith et al., 2001, 2004; Dou et al, 2003), but as yet, the role pig slurry amendments have to play in controlling leached losses has not been investigated. O' Flynn et al. (2012a, 2012b) examined the effectiveness and feasibility of different chemical amendments, added to pig slurry, in reducing P, SS and metal concentrations in a series of laboratory studies, conducted first at bench scale (O' Flynn et al., 2012a) and then using a laboratory rainfall simulator (O' Flynn et al., 2012b). In the latter study, O' Flynn et al. (2012b), found additions of alum, ferric chloride (FeCl_3) and poly-aluminium chloride (PAC) reduced total phosphorus (TP) and SS losses in surface runoff, without posing a significant risk of metal losses.

Although there has been much work done on the chemical amendment of surface applied pig slurry, there is an absence of work investigating any potential negative impact that this may have on N and carbon (C) losses and on greenhouse gas (GHG) emissions. Brennan et al. (2012) found in a plot study that chemical amendment of dairy cattle slurry with PAC reduced ammonium-N (NH_4^+ -N) runoff losses, but alum and lime led to increased NH_4^+ -N losses. All amendments reduced P losses in runoff, but had no effect on nitrate (NO_3^- -N) runoff losses. The Intergovernmental Panel on Climate Change (IPCC) (2007) estimates that

agricultural activities, including land application of animal manures, account for about 20% of the anthropogenic global warming budget, with emissions principally comprised of methane (CH₄) from enteric fermentation and manure management and nitrous oxide (N₂O) from N application to soils. The EU 2020 Climate and Energy Package and its associated Effort-Sharing Decision (Decision No 406/2009/EC) envisages reducing GHG emissions by 20% by 2020 across the whole of the EU. Whilst previous work has investigated the impact of chemical amendments to pig slurry to reduce P in runoff (O' Flynn et al., 2012a, 2012b), no study has investigated the impact of chemical amendment of pig slurry on GHG emissions.

Therefore, the aims of this laboratory study were to investigate if chemical amendment of pig slurry: (1) reduced leached losses of N, P and C from a low P index soil (2) resulted in changes to soil properties at different time intervals during the study period and (3) led to a reduction in GHG emissions over 28 d from the time of application.

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, Rep. of Ireland in September 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 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 in a 25-L drum inside a cold-room fridge at 10°C prior to testing. The TP and total

nitrogen (TN) were determined using persulfate digestion. Ammonium-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). Total carbon was measured using a nutrient analyser (Biotector, BioTector Analytical Systems Ltd, Ireland). Slurry pH was determined using a pH probe (WTW, Germany). Dry matter (DM) content was determined by drying at 105°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 1.

2.2 Pig slurry amendment

Amendments for the present study were chosen based on effectiveness of P sequestration and feasibility criterion (cost and potential environmental impediments) determined by O' Flynn et al. (2012a, 2012b). The amendment rates, 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 PAC (10 % Al_2O_3) applied at a rate of 0.72:1 [Al:TP]. Amendments were added to slurry in a 100-ml plastic cup and mixed for 10 s. The compositions of the amendments used are shown in Table 2.

2.3 Soil collection and analysis

A sample of the plough layer (top 0.2 m) of an acid brown earth soil was collected from a tillage farm in Fermoy, Co. Cork, Republic of Ireland. The site is typical of a free draining soil, underlain by a karstified limestone aquifer. Tillage soil was chosen, as this type of soil is

often of a lower P index and is more suitable for the landspreading of pig manure. The soil was air-dried, sieved (<2 mm) and thoroughly mixed. Soil samples (n=3) were oven dried at 40 °C for 72 h, crushed to pass a 2 mm sieve and analysed for Morgan's P (P_m, the national test used for the determination of plant available P in Ireland) using Morgan's extracting solution (Morgan, 1941). Soil total carbon (TC) and TN were determined by high temperature combustion using a LECO Truspec CN analyser (LECO Corporation, St. Joseph, MI, USA). Soil pH (n=3) was determined using a pH probe (WTW, Germany) and a 2:1 ratio of deionised water-to-soil. The STP of the sample used in the column and batch experiments was 3.21±0.29 mg L⁻¹ (making it a P index 2 soil according to S.I. No. 610 of 2010), total potassium (TK) of 41.8±3.00 mg L⁻¹, TC of 1.84±0.05 %, TN of 0.19±0.00 %, C:N ratio of 9.87±0.22, a pH of 6.26±0.13, an organic matter (OM) content of 4.68±0.14%. A low range STP tillage soil was chosen for this experiment to avoid the risk of background P from a high range STP soil 'masking' the effect of each treatment. A low range STP tillage soil was also chosen as present and future regulations will have the effect of making this type of land more preferable for pig slurry spreading in the future.

The particle size distribution was determined using a sieving and pipette method (B.S.1377-2; British Standards Institution (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 unstructured soil in the column and batch experiments consisted of 57% sand, 29% silt and 14% clay, giving it a sandy loam texture.

During any interaction with chemically amended slurry, the background soil P adsorption rate must also be considered and can be assessed in a batch experiment following the procedure outlined by Fenton et al. (2009). Ortho-phosphorus (PO₄³⁻-P) solutions (90 ml), synthesised

using dissolved potassium phosphate (KH_2PO_4) in distilled water, ranging in concentration from 4.1 to 28.9 mg P L^{-1} , were added to 5 g samples of soil and shaken for 24 h using an end-over-end shaker. Samples were passed through 0.45- μm syringe filters prior to being analysed colorimetrically for dissolved reactive phosphorus (DRP) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). A Langmuir isotherm was used to estimate the mass of P adsorbed per mass of the soil (McBride, 2000):

$$\frac{C_e}{x/m} = \frac{1}{ab} + \frac{C_e}{b} \quad [1]$$

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 dry weight of soil (g kg^{-1}), a is a constant related to the binding strength of molecules onto the soil, and b is the maximum adsorption capacity of the soil (g kg^{-1}). In conjunction with the P adsorption capacity of the soil, the equilibrium P concentration of the soil (EPC_0) (i.e. the point where no net desorption or sorption occurs) was derived using (Olsen and Watanabe, 1957):

$$S' = k_d C - S_0 \quad [2]$$

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 soil (mg L^{-1}). The mass of P adsorbed per unit dry weight of soil was 0.224 g P kg^{-1} and the soil's EPC_0 was 0.513 mg L^{-1} .

Soil water holding capacity (WHC) was determined according to Cassel and Nielsen (1986). Soil was placed on a funnel whose sides were covered with Whatman no. 2 filter paper, and distilled water was added to the soil until it became completely saturated. Saturated soil was weighed, oven-dried overnight at 105°C, and weighed again.

Water-filled pore space, which can impact on rates of denitrification in soil, was estimated in accordance with Haney and Haney (2010):

$$WFPS = \frac{WC * \rho_b}{n} \quad [3]$$

where ρ_b is bulk density and n is total porosity (mineral density was taken as 2.65 g cm⁻³).

Mineral N in soil (NH₄⁺-N, NO₃⁻-N and nitrite-N (NO₂⁻-N)) was determined at 0, 7 and 28 d after land application of pig slurry by adding 20 g of soil to 2 M KCl, shaking for 1 h, filtering through No. 2 Whatman filter paper, and testing using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Extra soil columns (n=3 for each treatment) were set up to allow sampling after 7 d for soil mineral N.

2.4 Experimental columns

The experiment was conducted in 0.3-m-deep and 0.104-m-internal diameter columns with a perforated stop-end inserted at the base to ensure that the soil remained free draining. A 0.05-m layer of gravel, with a grain size of 5 – 10 mm, was placed at the base of each column.

Sieved soil (< 2 mm), previously mixed with distilled water to achieve a water content (WC) of 26% (to replicate the average *in situ* field condition of the soil), was placed in 0.05 m-deep increments in each column, so as the average dry bulk density was approximately 1.1 g cm⁻³

(equivalent to field conditions) and the total depth of soil was 0.2 m. At each depth increment, soil was pressed along the wall of the column to avoid preferential flow (Bhupinder Singh, pers. comm.).

The following treatments were examined: (1) soil only with no slurry applied (2) soil with unamended slurry applied (the study control) and (3) soil receiving amended slurry. Slurry was spread at 19 kg TP, 90 kg TN, and 180 kg TC ha⁻¹. Columns were stored in a controlled environment for 8 mo at 10° C at 75% humidity, based on typical climatic conditions in Ireland (Walsh, 2012). All columns received 160 ml of distilled water wk⁻¹, applied twice weekly in two 80 ml increments over 2 h. This is equivalent to 980 mm of rainfall yr⁻¹, or 19 mm wk⁻¹, which would be in the mid-range of average annual rainfall amounts in Ireland (Walsh, 2012). This application rate remained constant for the duration of the study; however, actual rainfall rates will vary considerably over the course of a year. Drainage water leachate was collected in plastic containers *via* funnels positioned under the perforated stop-end of each column.

2.5 Leachate collection and analysis

The leachate from each column was composited and sampled weekly. Upon collection, samples were weighed and a subsample was passed through a 0.45-µm filter and analysed colorimetrically for DRP, NO₂⁻, NH₄⁺ and total oxidized nitrogen (TON) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Nitrate was calculated by subtracting NO₂⁻ from TON. Filtered and unfiltered subsamples were tested for total dissolved phosphorus (TDP) and TP using acid persulfate digestion. Particulate phosphorus (PP) was calculated by subtracting TDP from TP. Dissolved un-reactive phosphorus (DUP)

was calculated by subtracting DRP from TDP. Total nitrogen, total organic carbon (TOC) and total inorganic carbon (TIC) were measured using a nutrient analyser (Biotector, BioTector Analytical Systems Ltd, Ireland). Total carbon was calculated by adding TIC and TOC. Leachate pH was determined using a pH probe (WTW, Germany). This addressed the first aim of the study.

2.6 Destructive soil sampling

Soil columns were destructed after 1, 2, 3, 6 and 8 mo (n=3 for each treatment, at each time period) and tested for WC, OM, pH, water extractable P (WEP), P_m, TN and TC. Before analyses, each column was divided into 3 layers (0 to 0.05 m, 0.05 to 0.1 m, and 0.1 to 0.2 m from the surface). Organic matter content of the soil was determined using the LOI test (B.S.1377-3; BSI, 1990b). Soil pH was determined using a pH probe (WTW, Germany) and a 2:1 ratio of deionised water-to-soil. Water extractable P was measured by shaking 5 g of soil in 25 ml of distilled water for 30 min, filtering through a 0.45- μ m syringe filter, prior to being analyzed colorimetrically for DRP (McDowell and Sharpley, 2001) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Morgan's P was determined using Morgan's extracting solution (Morgan, 1941). Soil TC and TN were determined for the middle layer only in each column (0.05 to 0.1-m-depth) by high temperature combustion using a LECO Truspec CN analyser (LECO Corporation, St. Joseph, MI, USA). This addressed the second aim of the study.

2.7 Greenhouse gas emissions

Direct GHG emissions (N₂O, carbon dioxide (CO₂) and CH₄) were analyzed over a 28-d period in accordance with Troy et al. (2013). Samples were taken on the day of slurry application (day 1) and subsequently on days 2, 3, 4, 5, 6, 7, 9, 11, 13, 15, 19, 23 and 28. The top of the PVC columns were sealed using a rubber stopper. A sample of the air in the headspace above the columns was taken through a rubber septum using a polypropylene syringe with a hypodermic needle. The sample was immediately transferred into a pre-evacuated 7-ml screw cap septum vial. Samples were taken at 0, 5, 10 and 20 min after the sealing of columns with a rubber stopper. After this period, the rubber stopper was removed. Nitrous oxide, CO₂ and CH₄ concentrations were analysed using a gas chromatograph (Varian CP 3800 GC, Varian, USA) fitted with a ⁶³Ni electron capture detector (ECD) for N₂O analysis, a thermal conductivity detector (TCD) for CO₂ analysis and a flame ionization detector (FID) for CH₄ analysis. During the analysis, 0.7 ml of a sub-sample from each vial was drawn and injected first into a magnesium perchlorite (14-22 mesh) packed pre-column to remove any moisture, followed by a 3-m-long, 3-mm-outside diameter stainless steel column packed with Poropak Q (80/100 mesh). The column oven and injector temperature were both 60°C and the detector temperature was 350°C. Argon (BOC Gases, Ireland), flowing at 35 ml min⁻¹, was used as a carrier gas. Samples were fed into the system by a Combi-Pal automatic sampler (CTC Analysis, Switzerland) controlled by computer software. Two-thirds of the injected sample was split to the ECD detector and one-third to the TCD and FID in series. This allowed the simultaneous measurement of all three gases from the one sample. Areas under the peaks were integrated using Star Chromatography Workstation (Varian, USA). Fluxes were calculated from the change in headspace concentration over measured period using:

$$\frac{dGas}{dt} * 10^x * \frac{V_{chamber} * p * 100 * MW}{R * T} * 10^y * \frac{1}{A} \quad [4]$$

where: $dGas$ is measured in ppm or ppb to get concentration at a certain point in time or ppm h^{-1} or ppb h^{-1} to get the change in concentration over time; 10^x is a recalculation (10^{-6} if starting from ppm or 10^{-9} if starting from ppb); $V_{chamber}$ is the volume of the chamber used; p is atmospheric pressure; MW is the molecular weight either of N or N_2O , depending of which compound in which the emissions are expressed; R is a gas constant, $8314 \text{ J mol}^{-1} \text{ K}^{-1}$; T is temperature in Kelvin; 10^y is a recalculation (10^3 if the results are expressed in mg or 10^6 if in μg); and A is the area of the chamber. The fluxes were then converted into $\text{mg m}^{-2} \text{ d}^{-1}$. Mean daily emissions rates were calculated for each replicate by interpolation of values in between the measurement days using arithmetic means (Velthof and Oenema, 1995; Flechard et al., 2007). This addressed the third aim of the study.

2.8 Statistical analysis

The data was analysed in SPSS 20 (IBM, 2011) using a general linear model. Mean values of: WC; OM; soil P, N and C species; soil pH; leachate P, N and C species; leachate pH; and GHGs were analysed in a multivariate Tukey analysis when soil-only, slurry-only (the study control), and slurry treated with alum, PAC and FeCl_3 were applied. Data met the normal distributional assumptions required. Probability values of $p > 0.05$ were deemed not to be significant.

3. Results

3.1. Water content, organic matter and soil pH

The WHC of the soil was found to equate to a WC of 53%. In general, there were no significant differences observed in WC between treatments, apart from at 1 mo in the top soil layer, where the soil-only treatment had a WC of $30.33 \pm 0.24\%$ (data not shown).

Comparatively, at the same time, slurry-only, alum, FeCl_3 and PAC treatments had WCs of $31.76 \pm 0.44\%$, $32.45 \pm 0.35\%$, $31.89 \pm 0.78\%$, and $32.13 \pm 0.39\%$. Water contents increased with depth: WCs in the top soil layer were generally between 30 and 33%, between 31 and 34% in the middle layer, and between 35 and 38% in the bottom layer. These equated to water-filled pore space (WFPS) values of between 56 and 62% in the top layer, between 58 and 64% in the middle layer, and between 65 and 72% in the bottom layer. Organic matter (generally between 4.3 and 4.7%) and soil pH (between 6 and 6.5) were not significantly affected by treatment, depth or time.

3.2. Nitrogen leachate and soil properties

There were no statistically significant differences between treatments for TN in soil (Table 3). No significant differences between treatments were observed for the N in leachate water, which mainly comprised NO_3^- . The amount of NO_3^- leached increased rapidly until wk 2, before it reduced gradually thereafter (Fig. 1 c). Approximately 95% of TN leached from the columns over the duration of the studies was in the form of NO_3^- , with roughly 0.2% in the form of NO_2^- and 0.3% in the form of NH_4^+ . The C:N ratio for all treatments at all destructive periods was between 9 and 10 (Table 3). Nitrite loads peaked between wks 10 and 26 (Fig. 1 b).

At all times, mineral N in soil comprised less than 2% of soil TN. Seven days after application, soil NH_4^+ was observed to be highest for the alum and FeCl_3 treatments (83.7

and 79.3 g $\text{NH}_4^+\text{-N kg}^{-1}$ soil, respectively). This compared with values of 44.0 and 48.9 g $\text{NH}_4^+\text{-N kg}^{-1}$ soil for soil-only and slurry-only, respectively.

3.3. Nitrous oxide emissions

Nitrous oxide emissions from the soil-only treatment remained fairly constant throughout the 28-d study (Fig. 2 a), with cumulative emissions of 22 ± 8 mg $\text{N}_2\text{O-N m}^{-2}$. Application of pig slurry led to an increased cumulative release of N_2O . Cumulative emissions across all N-applied treatments were high, ranging approximately from 60 to 200 mg $\text{N}_2\text{O-N m}^{-2}$. The highest cumulative losses of 188 ± 86 mg $\text{N}_2\text{O-N m}^{-2}$ was observed for FeCl_3 -amended slurry and this was the only treatment statistically significantly different ($p=0.008$) to soil-only, but was not statistically significantly different to any other treatment. Cumulative emissions from all treatments remained relatively constant between 4 and 7 d after application of slurry, at which point they increased more rapidly, although not significantly, and continued to rise until the end of the study. However, N_2O losses from FeCl_3 -amended slurry were at all times greater than all other treatments. Alum and PAC-amended slurries both had less, but not statistically significantly different, N_2O losses than unamended slurry, but more than soil-only.

3.4. Phosphorus leachate and soil properties

There were no significant differences in the quantity of P leached between treatments, with the majority of TP made up of TDP for all treatments. Particulate phosphorus comprised approximately 30% of the TP load in all cases.

In general, there were no significant differences in levels of Pm and WEP between treatments in the bottom two soil layers (Table 3). However, in the top soil layer, application of unamended slurry resulted in increased Pm and WEP, which were significantly different ($p < 0.05$) to the soil-only columns at all destructive periods (Table 3). Levels of Pm and WEP in the top soil layer were both reduced by the application of amended slurry to levels not significantly different to soil-only columns (Table 3).

3.5. Carbon leachate

The average cumulative amount of TOC and TIC leached is shown in Fig. 3 a. The average TC leached from the soil-only columns was 217.3 mg. This increased to 253 mg from columns with unamended slurry, with reduced amounts of TC leached from columns treated with amended slurry. However, there were no statistically significant differences for TC loads between treatments. There was an increase in loads of TC leached from wk 1 to wk 2 (Fig. 3 b); however, this was due to lower leachate volumes during wk 1 than wk 2, rather than any changes in concentration. The loads of TC leached then decreased after wk 2 until the end of the study, during which time there was no significant change in flows.

3.6. Carbon emissions

Emissions of CO₂ followed a similar trend to N₂O emissions (Fig. 2 b). The soil-only treatment had the lowest emissions, with cumulative losses of 36±4 g CO₂-C m⁻². Losses increased upon application of slurry, but were only statistically significantly different ($p = 0.008$) in the case of FeCl₃-amended slurry, which had cumulative losses of 106±23 g CO₂-C m⁻². However, this was not statistically significantly different to any other unamended

or amended slurry treatment. Alum and PAC-amended slurries had less, but not statistically significant different, losses than unamended slurry. Methane losses were highly variable (Fig. 2 c), but no treatment had significantly higher losses than the soil-only treatment. After 5 days, all treatments either gained or lost CH₄, with FeCl₃-amended slurry acting overall as a net sink with cumulative losses of -13±7 mg CH₄-C m⁻², whilst PAC-amended slurry had cumulative losses of 13±6 mg CH₄-C m⁻².

4. Discussion

4.1 Nitrogen leachate and soil properties

Denitrification is the mainly microbial reduction of NO₃⁻-N to the gaseous products nitric oxide (NO), N₂O, or inert di-nitrogen (N₂). Some studies have shown that the highest rates of denitrification occur in the upper soil horizon (Kustermann et al., 2010; Jahangir et al., 2012), the extent of which depends on WC and WFPS. Soil WC can impact on many different soil processes such as mineralization, leaching, plant uptake and denitrification (Porporato et al., 2003).

The early peak in NO₃⁻ loss may be due to the drying and re-wetting during column construction, which could have caused a surge in microbial activity and C and N mineralisation (Van Gestel et al., 1991; Bengtsson et al., 2003). This may also have led to an early peak in leachate NH₄⁺ (Fig. 1 a). Once rewetting was complete, WFPS levels were between 65 and 72% in the bottom layer. At WFPS levels of over 60%, denitrification may take place, releasing nitrogen gas (N₂) and N₂O into the atmosphere (Porporato et al., 2003). Aerobic microbial activity and nitrification is also reduced in these anaerobic conditions

where denitrification is facilitated (Poporato et al., 2003; Rivett et al., 2008). The fractions of NO_2^- , NO_3^- and NH_4^+ in the leachate would seem to indicate that almost complete nitrification occurred, and also led to the drop in NO_3^- levels after wk 2. This hypothesis was also supported by the C:N ratios present (Table 3). Soil with C:N ratios below 20 can be characterised as having a surplus of available NH_4^+ for nitrification (Bengtsson et al., 2003). The peak in NO_2^- between wks 10 and 26 may have been due to a delay in reduction of NO_2^- during denitrification down to the preference of denitrifiers for NO_3^- , even when both are present (Rivett et al., 2008).

High NH_3^+ volatilization may occur after land application of pig slurry, with over 60% of total losses occurring in the first 10 h after application (Gordon et al., 2001; Rochette et al., 2001). It would appear in the current study that a large amount of volatilization occurred from both amended and unamended slurry treatments with little unvolatilised inorganic N remaining, which is in agreement with previous studies (Morvan et al., 1997; Hoekstra et al., 2010; Hoekstra et al., 2011). Indeed, these rates of volatilization may represent a loss of 50-80% of total ammoniacal nitrogen from landspread slurry over a 10-d period (Misslebrook et al., 2005a, 2005b; Meade et al., 2011). The slurry organic fraction was undetectable in leachate or soil (Table 3) due to the large background amounts of soil inorganic N, which was a result of the occurrence of mineralization. Unlike the present study, which found no significant difference between NO_3^- losses from columns with and without slurry spread on them, Daudén et al. (2004) found that drainage NO_3^- concentrations and loads consistently increased with increasing amount of N applied when landspreading pig slurry and mineral fertiliser between 275 and 1487.5 kg N ha⁻¹. However, the spreading rate used by Daudén et al. (2004) was much higher than in the present study (90 kg N ha⁻¹), and in that study, pig slurry was incorporated into soil to minimise volatilization losses.

4.2 Nitrous oxide emissions

The increased cumulative release of N₂O after slurry application was as expected (Velthof et al., 2003). The cumulative N₂O emissions across all N-applied treatments represented a loss of between 1% and 3% of applied total ammoniacal N for a 28-d period. This was a higher emission factor than the IPCC default emission factor of 1% (IPCC, 2006). Generally, higher emission factors would not be associated with free-draining soil such as the one used in this study (Abdalla et al., 2009; Rafique et al., 2011). However, emission factors associated with slurry application have previously been observed to be higher than the default values and this may be related to the simultaneous application of a labile C source, which increases microbial activity (Dendooven et al., 1998; Sherlock et al., 2002). Nitrous oxide is produced by both nitrification and denitrification (Chadwick et al., 2011), and can be influenced by oxygen availability, soil WC, soil temperature, soil NO₃⁻ and organic carbon content (Section 4.4) (Velthof et al., 2003). The drying and rewetting of the soil during construction provided conditions which facilitated C and N mineralisation and denitrification, would also have facilitated N₂O release to the atmosphere (Porporato et al., 2003).

The increase in N₂O emissions associated with FeCl₃ addition may be explained as a result of ammonia volatilisation abatement. The difference in soil NH₄⁺ levels between treatments 7 d after application was due to a reduction in volatilisation, possibly resulting from a reduction in slurry pH upon amendment addition. Previous work has observed that volatilisation may be reduced upon FeCl₃ addition, principally due to a reduction in slurry pH (Molloy and Tunney, 1983).

4.3 Phosphorus leachate and soil properties

Unlike previous runoff studies (O' Flynn et al., 2012b), in which spreading of pig slurry led to a large increase in all types of P in runoff compared to runoff from soil-only, there were no significant differences in the quantity of P leached between treatments. The fraction of TP load made up of TDP was less when compared to O' Flynn et al. (2012b), who found PP in runoff comprised, on average, 45% of TP. This is in agreement with McDowell et al. (2004), who found that more TP was lost as PP in overland than subsurface flow due to the higher kinetic energy and erosive power of high-frequency storms. Loss of P in subsurface flow is generally less than that in runoff, and will decrease as the degree of soil–water contact increases, due to sorption by P-deficient subsoils (Haygarth et al., 1998; McDowell et al., 2004). Although a soil with a low Pm ($3.21 \pm 0.29 \text{ mg L}^{-1}$) was used in this experiment, its high adsorption capacity for P ($0.224 \text{ g P kg}^{-1}$) and low EPC_0 (0.513 mg L^{-1}) facilitated adsorption of P during leaching.

The same amendments and application rates as used in the present study were also used by O' Flynn et al. (2012a), who achieved reductions of between 95 and 99% in the WEP of slurry. Dao (1999) amended stockpiled cattle manure with caliche, alum and flyash in an incubation experiment, and reported WEP reductions in amended manure, compared to the study control, of 21, 60 and 85%, respectively. Similarly, in a study that examined the effect of soil P level in a silt loam soil which was incubated at 25°C, Kalbasi and Karthikeyan (2004) reported that applications of alum and FeCl_3 -amended slurry to soil decreased soil WEP. In the present study, due to the regular application of 160 ml water wk^{-1} , which led to the downward leaching of P from the slurry, both Pm and WEP levels in the columns spread with unamended slurry reduced to levels closer, but still significantly different ($p < 0.05$), to soil-

only and amended slurry columns. This P was adsorbed by the soil's high adsorption capacity for P, but was not detected by WEP or Pm analysis.

4.4 Carbon leachate and emissions

The decrease in loads of TC leached after wk 2 may have been due to the increased mineralization of C and N, which may have been the cause of increased losses of CO₂ to the atmosphere. This loss of CO₂ to the atmosphere may also be the reason that there were statistically no significant differences between treatments for TC in soil (Table 3). In addition, organic carbon can act as an electron donor to facilitate the occurrence of denitrification when anaerobic conditions are present (Rivett et al., 2008).

The addition of manure slurries to soil has been shown to cause an increase in microbial activity and CO₂ emissions (Bol et al., 2004; Dumale et al., 2009; Cayuela et al., 2010). The increased CO₂ losses from unamended or amended slurry treatments were in agreement with the hypothesis that these losses were the cause for no statistically significant differences between slurry treatments for TC in soil (Table 3).

After land application, CH₄ emissions are generally of minor importance compared to N₂O emissions (Wulf et al., 2002a, 2002b), as CH₄ emissions from enteric fermentation and during slurry storage are much more important (Chadwick et al., 2000). This is due to CH₄ being produced by decomposition of OM in faecal matter under anaerobic conditions. After landspreading, OM is oxidised to CO₂ and H₂O in the aerobic conditions present. Mineral grassland soils are known to generally be a CH₄ sink, due to either oxidation of CH₄ to CO₂ in soils or incorporation into microbial biomass, with uptake rates ranging from 0.5 – 3.3 mg

$\text{CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Mosier et al., 1991; Dobbie et al., 1996; Saggar et al., 2008). The results from the present study show that no additional risk to CH_4 emissions is posed by the chemical amendment of pig slurry.

4.5 Outlook for use of chemical amendment as a mitigation measure

Increased intensification of pig farming activities, along with legislation reducing the amount of land onto which pig farmers may apply slurry, has meant that the pig industry is under increasing pressure to reconcile production and water quality objectives. Land application of pig slurry is currently the most cost-efficient method for its disposal. In Ireland, the pig industry is concentrated in a small number of areas, with typically high stocking rates. Therefore, the disposal of slurry in a cost-effective and environmentally responsible way is a serious issue for farmers.

This study demonstrates that amendments previously selected on the basis of ability to reduce runoff P (O' Flynn et al., 2012a,b), may be used without posing a negative impact on leachate, soil properties, and GHG emissions.

Based on the results of the current study and also previous work by the authors comparing cost (O' Flynn et al., 2012a) and surface runoff losses (O' Flynn et al., 2012b), PAC appears to be the most suitable amendment with which to chemically amend pig slurry. Ferric chloride resulted in increased N_2O and CO_2 losses, whereas alum and PAC resulted in reduced, but not significantly different, losses to slurry-only. Poly-aluminium chloride performed best in overall removal of runoff P and SS (O' Flynn et al., 2012b). There was little difference between leachate losses and soil effects from alum and PAC-amended slurry,

although this study only included one soil type. The current study used a low STP soil so as to avoid the risk of background P from a high range STP soil ‘masking’ the effect of each treatment. However, future work must examine a wide variety of soil types, including high STP soils. These amendments must also be examined at field-scale, and include repeated application and incorporation. Costs were comparable (O’ Flynn et al., 2012a), with estimated costs of amending and spreading amended slurry of €3.33 and €3.69 m⁻³ for alum and PAC, respectively, in comparison to €1.56 m⁻³ to spread unamended slurry.

In the current study, reductions were not adequate to satisfy the EU 2020 Climate and Energy Package of reducing GHG emissions by 20% across the whole of the EU by 2020. It has however, been shown that some reductions are possible, and future work must be carried out to identify if more significant reductions in GHG emissions is possible at different application rates.

At present, there is no provision in legislation for chemical amendments to be used as a mitigation measure in the land application of pig slurry, but if they are to be utilised, a regulatory framework will need to be introduced by the relevant bodies.

5. Conclusions

Chemical amendment of land applied pig slurry can reduce P in runoff without any negative impact on nutrient leaching. Furthermore, there were no significant differences between treatments for N and C in leachate or soil, indicating no deleterious impact on reactive N emissions or soil C cycling. Chemical amendment posed no significant change to GHG emissions from pig slurry, and in the cases of alum and PAC, reduced cumulative N₂O and

CO₂ losses. Moreover, increased N₂O emissions associated with FeCl₃ addition were likely to be due to a reduction in ammonia volatilisation, a theory supported by an increase in soil NH₄⁺ concentrations.

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Figure Captions

Figure 1. Average weekly loads of ammonium a) nitrite b) and nitrate c) leached column⁻¹ (\pm standard deviation).

Figure 2. Cumulative gaseous emissions of N₂O-N (a) CO₂-C (b) and CH₄-C (c) from columns at each sampling period (\pm standard deviation).

Figure 3. Cumulative loads of total organic carbon (TOC) and total inorganic carbon (TIC) leached over the duration of the experiment a) and weekly loads of total carbon leached from columns b) (\pm standard deviation).

Table 1. 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	TC	NH ₄ ⁺ -N	pH	DM	Reference
(mg L ⁻¹)					(%)	
620±32	2940±156	5860±80	1739 ±8	7.51 ± 0.08	3.02± 0.24	The present study
800	4200					S.I. No. 610 of 2010
1630	6621				5.77	McCutcheon, 1997 ^a
900±7	4600±21				3.2±2.3	O' Bric, 1991 ^a

TP, total P; TN, total N; TK, total K; DM, dry matter. ^aValues changed to mg L⁻¹ assuming densities of 1 kg L⁻¹.

Table 2. Characterisation of amendments used in this study (O' Flynn et al., 2012a, 2012b)

Amendment		Alum	Ferric Chloride	PAC
		8% Al ₂ O ₃	38% FeCl ₃	10 % Al ₂ O ₃
pH		1.25		1.0 – 3.0
WEP	mg kg ⁻¹	0		
Al	%	4.23		
Fe	%	<0.01	38	
As	mg kg ⁻¹	1	<2.8	<1.0
Cd	mg kg ⁻¹	0.21	<3.4	<0.2
Cr	mg kg ⁻¹	2.1	<48	<2.0
Cu	mg kg ⁻¹		<65	
Mn	mg kg ⁻¹		<1370	
Ni	mg kg ⁻¹	1.4	<48	<1.0
Pb	mg kg ⁻¹	2.8	<14	<2.0
Sb	mg kg ⁻¹		<2.8	<1.0
Se	mg kg ⁻¹		<2.8	<1.0
Hg	mg kg ⁻¹		<0.7	<0.2

Table 3. Average soil phosphorus, nitrogen and carbon contents by sampling time and depth.

	Month	Depth (mm)	Treatment				
			Soil Only	Slurry	Alum	FeCl ₃	PAC
Morgan's P (mg L ⁻¹)	1	0-50	3.53 ^a	7.79 ^c	4.19 ^{ab}	4.64 ^b	4.40 ^{ab}
		50-100	3.69 ^a	3.80 ^a	3.75 ^a	3.69 ^a	3.68 ^a
		100-200	3.53 ^a	3.99 ^a	3.79 ^a	3.95 ^a	3.84 ^a
	2	0-50	3.84 ^a	6.12 ^b	4.41 ^a	4.61 ^a	4.52 ^a
		50-100	4.02 ^a	4.03 ^a	3.85 ^a	3.80 ^a	3.99 ^a
		100-200	4.14 ^a	4.31 ^a	3.88 ^a	3.86 ^a	4.08 ^a
	3	0-50	3.19 ^a	6.28 ^c	4.22 ^b	4.55 ^b	4.28 ^b
		50-100	3.14 ^a	3.17 ^a	3.50 ^a	3.60 ^a	3.39 ^a
		100-200	3.35 ^a	3.55 ^a	3.71 ^a	3.78 ^a	3.67 ^a
	6	0-50	2.69 ^a	4.60 ^c	3.44 ^{ab}	4.18 ^{bc}	3.52 ^{ab}
		50-100	3.22 ^a	3.41 ^a	3.21 ^a	3.62 ^a	3.10 ^a
		100-200	3.51 ^a	3.67 ^a	3.65 ^a	3.61 ^a	3.28 ^a
8	0-50	2.17 ^a	3.42 ^c	2.63 ^{ab}	3.00 ^{bc}	3.38 ^c	
	50-100	2.44 ^a	2.39 ^{ab}	2.67 ^{ab}	2.95 ^{ab}	3.16 ^b	
	100-200	2.66 ^a	3.14 ^a	3.01 ^a	3.38 ^a	3.66 ^a	
WEP (mg kg ⁻¹)	1	0-50	0.54 ^a	1.13 ^b	0.49 ^a	0.57 ^a	0.59 ^a
		50-100	0.56 ^a	0.58 ^a	0.54 ^a	0.58 ^a	0.57 ^a
		100-200	0.64 ^a	0.56 ^a	0.57 ^a	0.60 ^a	0.54 ^a
	2	0-50	0.51 ^a	0.99 ^b	0.57 ^a	0.57 ^a	0.55 ^a
		50-100	0.49 ^a	0.47 ^a	0.49 ^a	0.45 ^a	0.50 ^a
		100-200	0.50 ^a	0.46 ^{ab}	0.39 ^b	0.43 ^{ab}	0.45 ^{ab}
	3	0-50	0.62 ^a	1.06 ^b	0.69 ^a	0.71 ^a	0.73 ^a
		50-100	0.65 ^a	0.66 ^a	0.61 ^a	0.67 ^a	0.62 ^a
		100-200	0.64 ^a	0.70 ^a	0.65 ^a	0.63 ^a	0.62 ^a
	6	0-50	0.54 ^a	0.87 ^b	0.60 ^a	0.63 ^a	0.52 ^a
		50-100	0.54 ^a	0.55 ^a	0.50 ^a	0.52 ^a	0.49 ^a
		100-200	0.49 ^a	0.51 ^a	0.47 ^a	0.47 ^a	0.44 ^a
8	0-50	0.58 ^a	0.79 ^b	0.55 ^a	0.56 ^a	0.62 ^{ab}	
	50-100	0.58 ^a	0.62 ^a	0.55 ^a	0.53 ^a	0.57 ^a	
	100-200	0.55 ^a	0.61 ^a	0.58 ^a	0.57 ^a	0.56 ^a	
TC (%)	1	50-100	1.70 ^a	1.73 ^a	1.86 ^a	1.69 ^a	1.74 ^a
	2	50-100	1.78 ^a	1.73 ^a	1.77 ^a	1.76 ^a	1.68 ^a
	3	50-100	1.72 ^a	1.73 ^a	1.74 ^a	1.84 ^a	1.68 ^a
	6	50-100	1.81 ^a	1.78 ^a	1.74 ^a	1.79 ^a	1.66 ^a
	8	50-100	1.75 ^a	1.73 ^a	1.73 ^a	1.79 ^a	1.75 ^a
TN (%)	1	50-100	0.18 ^a	0.18 ^a	0.20 ^a	0.19 ^a	0.19 ^a
	2	50-100	0.18 ^a	0.18 ^a	0.18 ^a	0.19 ^a	0.18 ^a
	3	50-100	0.18 ^a	0.18 ^a	0.18 ^a	0.19 ^a	0.18 ^a
	6	50-100	0.19 ^a	0.19 ^a	0.18 ^a	0.18 ^a	0.18 ^a
	8	50-100	0.19 ^a	0.19 ^a	0.18 ^a	0.18 ^a	0.18 ^a
C:N Ratio	1	50-100	9.53 ^a	9.39 ^a	9.32 ^a	9.07 ^a	9.30 ^a
	2	50-100	9.73 ^a	9.89 ^a	9.69 ^a	9.41 ^a	9.30 ^a
	3	50-100	9.54 ^a	9.61 ^a	9.51 ^a	9.80 ^a	9.39 ^a
	6	50-100	9.38 ^a	9.43 ^a	9.78 ^a	9.78 ^a	9.32 ^a
	8	50-100	9.31 ^a	9.35 ^a	9.79 ^a	10.04 ^a	9.76 ^a

^{abc} Means in a row, which do not share a superscript, were significantly different ($p < 0.05$)

Fig 1.

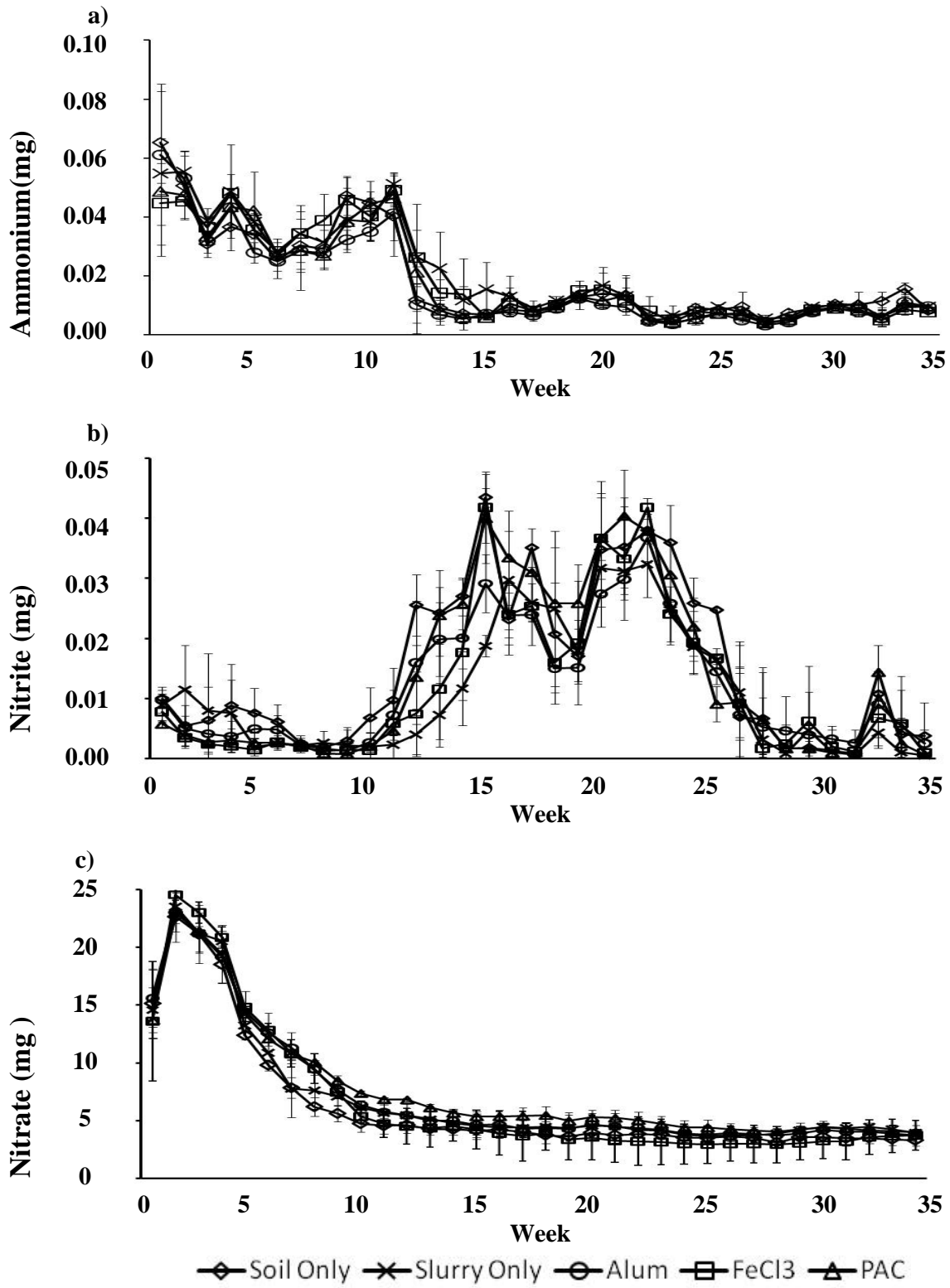


Fig 2.

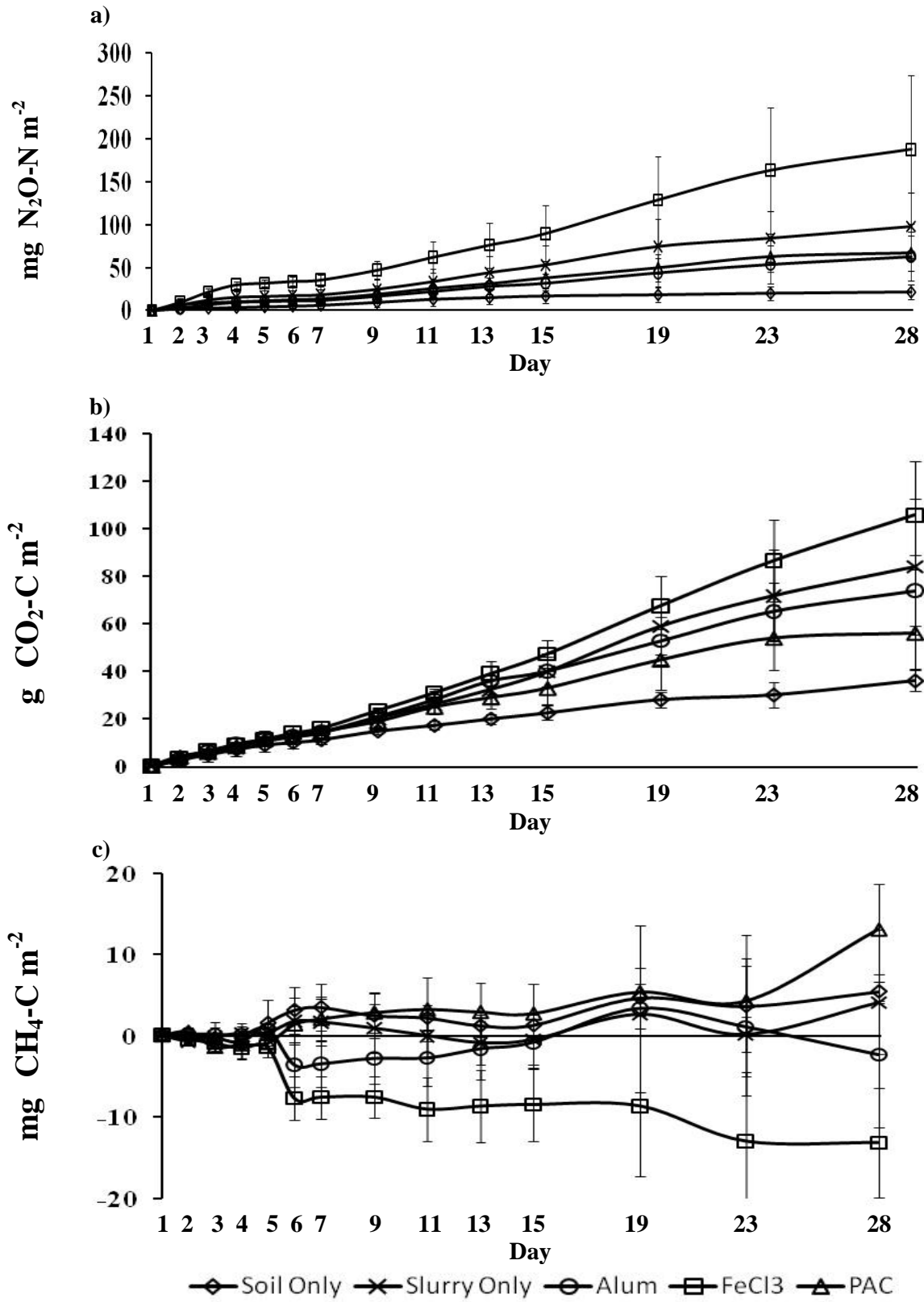


Fig 3.
a)

