NATIONAL UNIVERSITY OF IRELAND, GALWAY

THE IMPACT OF CHEMICALLY AMENDED PIG SLURRY ON SURFACE RUNOFF, LEACHATE AND GREENHOUSE GASSES

Cornelius J. O' Flynn, B.E. (Hons), B. Eng. (Ord), H. Cert.

Research Supervisors:

Dr. Mark G. Healy, Civil Engineering, NUI Galway

Dr. Owen Fenton, Teagasc, Johnstown Castle, Wexford

Professor Padraic E. O'Donoghue, Civil Engineering, NUI Galway

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Abstract

In Ireland, the pig industry is concentrated in a small number of counties. Pig farms typically have a high stocking rate. Therefore, the disposal of slurry in a cost-effective and environmentally-responsible way is a serious issue for farmers. Slurry is commonly applied to land, but this may not be possible if the land is at, or approaching, phosphorus (P) saturation. As pig farmers dispose of slurry in the vicinity of their properties, most of the nearby land is at P saturation, so alternative treatment methods need to be utilised (e.g. constructed wetlands, anaerobic digestion, filtration) or the slurry needs to be transported to another location. These alternatives are not currently financially viable in Ireland. Existing legislation (S.I. 610 of 2010) and recent changes in the implementation of legislation governing the timing and quantities of slurry that may be applied to land, means that pig farmers will no longer be able to exceed the maximum legal application rate to land (from January 2017). European policy aiming to intensify pig production will only accentuate this problem. If pig farmers are forced, in exceptional circumstances, to land apply slurry to unsuitable land, surface and subsurface losses of nutrients and suspended solids (SS) may occur. This could be potentially problematic if the land is located in a critical source area (CSA), an area that is highly likely to pollute receiving waters.

In these circumstances, a possible novel solution is to chemically amend the pig slurry prior to landspreading. This would mean that pig farmers may, in exceptional circumstances, utilise the land in the vicinity of their farms for landspreading, without releasing excessive nutrients and SS into receiving waters. However, knowledge gaps exist concerning the type of amendments to be used, the characteristics of the soil on which they can be most effectively used, and their impact on incidental (short-term) and chronic (long-term) losses of nutrients, SS and greenhouse gas (GHG) to surface and subsurface water and the atmosphere. Therefore, the aims of this project were to: (1) identify the most appropriate chemical amendments, and their addition rates, to reduce P losses in runoff from pig slurry based on effectiveness, cost and feasibility; (2) investigate the impacts of these chemical amendments on nutrient losses in leachate, soil properties and GHG emissions; and (3) identify suitable soil types on which to landspread chemically-amended pig slurry.

Laboratory bench-scale experiments were designed to identify the amendments which had the potential to reduce P in overland runoff and to quantify the stoichiometric rates at which to add them to the slurry. Based on effectiveness, cost and feasibility, the amendments identified were alum, which reduced dissolved reactive phosphorus (DRP) in overlying water by 86%, poly-aluminium chloride (PAC) (73%) and ferric chloride ($FeCl_3$) (71%). Following these bench-scale experiments, rainfall simulation experiments were conducted to quantify the impact of chemical amendments to slurry on surface runoff losses at various time intervals from the time of application. Poly-aluminium chloride performed best in these experiments. For the first time, the effect of these amendments on GHG emissions, soil properties and leachate was also examined. Chemical amendment did not adversely affect GHG emissions, soil properties or leachate from pig slurry, but $FeCl_3$ increased nitrous oxide (N_2O) and carbon dioxide (CO_2) losses. Finally, a 3-mo incubation experiment was conducted using a range of soil types to examine the effect of amendments on the long-term plant availability of P in soil and P solubility. Alum reduced more water extractable P than PAC, but also resulted in less plant available P. Considering cost, surface runoff and subsurface leachate losses, GHG emissions and impacts on soil chemistry, PAC was found to be the most suitable amendment with which to chemically amend pig slurry.

There is the potential, in combination with existing programmes of measures, to employ chemical amendment as a measure to mitigate the environmental impact arising from the landspreading of pig slurry. This should be conducted in targeted areas of the CSA and should take into account soil type and its chemical properties. Before implementation, these tests must first be validated in long-term testing at field-scale over a wide variety of soil types, and include repeated application and incorporation. 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.

Declaration

This dissertation is the result of my own work, except where explicit reference is made to the work of others, and has not been submitted for another qualification to this or any other university.

Cornelius O' Flynn

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Abbreviations

AAU	Agricultural Area Used
AD	Anaerobic digestion
AEOS	Agri-Environment Options Scheme
Al	Aluminium
$AlCl_3$	Aluminium chloride
Al-WTR	Aluminium-based water treatment residuals
C	Carbon
Ca	Calcium
$Ca(OH)_2$	Lime
CH_4	Methane
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon dioxide
CSA	Critical source area
Cu	Copper
CW	Constructed wetland
DM	Dry matter
DP	Dissolved phosphorus
DPS	Degree of phosphorus saturation
DRP	Dissolved reactive phosphorus
DUP	Dissolved un-reactive phosphorus
EC	European Commission
ECD	Electron capture detector
EPA	Environmental Protection Agency
EPC_0	Equilibrium phosphorus concentration
EU	European Union
Fe	Iron
$FeCl_3$	Ferric chloride
FGD	Flue gas desulphurization by-product
FID	Flame ionisation detector
FWMC	Flow-weighted mean concentration
FWS	Free water surface

GHG	Greenhouse gas
H_2	Hydrogen gas
H_2S	Hydrogen sulphide
ICP	Inductively-coupled plasma
ICW	Integrated Constructed Wetland
IPCC	Intergovernmental Panel on Climate Change
K	Potassium
LOI	Loss on ignition
M3	Mehlich 3
Mg	Magnesium
Mn	Manganese
MRP	Molybdate reactive phosphorus
N	Nitrogen
N_2	Di-nitrogen
N_2O	Nitrous oxide
NAP	National Action Programme
N_r	Reactive nitrogen
NH_3^+	Ammonia
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
OM	Organic matter
P	Phosphorus
PAC	Poly-aluminium chloride
Pm	Morgan's P
POM	Programmes of Measures
PP	Particulate phosphorus
RE	Rainfall event
REPS	Rural Environmental Protection Scheme
SRP	Soluble reactive phosphorus
SS	Suspended sediment
SSF	Subsurface flow
STP	Soil test phosphorus

TC	Total carbon
TCD	Thermal conductivity detector
TDP	Total dissolved phosphorus
TI	Time interval
TIC	Total inorganic carbon
TK	Total potassium
TN	Total nitrogen
TOC	Total organic carbon
TON	Total oxidized nitrogen
TP	Total phosphorus
WC	Water content
WEP	Water extractable phosphorus
WFD	Water Framework Directive
WFPS	Water-filled pore space
WHC	Water holding capacity
Zn	Zinc

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Chapter 1

Introduction

1.1 Pig industry in Europe and Ireland

There are approximately 149 million pigs in the European Union (EU) (Eurostat, 2013) and, in 2011, the pig industry accounted for 8.7% (€33 billion) of the EU's overall agricultural output (Eurostat, 2012). There are approximately 1.57 million pigs in the Republic of Ireland (CSO, 2012 a), including 145,700 breeding pigs, which produce almost 3 million tonnes of liquid pig manure annually. Agriculture is an important industry in the Republic of Ireland, where 65% of land use is devoted to agricultural enterprises (CSO, 2012 b). The total number of people employed in the pig sector in the Republic of Ireland is thought to be in the region of 7,500, with more than 1,200 employed directly at farm level (Teagasc, 2008). The pig industry had outputs with an estimated value of €432.7 million in 2012 - an increase of 9.8% (€39 million) on 2011 figures (CSO, 2012 c), and, in 2011, it made up over 0.2% of Ireland's Gross Domestic Product (CSO, 2012 d).

The Republic of Ireland's overall density of pig production, expressed as Agricultural Area Used (AAU), is 25.7 ha sow^{-1}, which is low compared with other EU states e.g. the Netherlands at 1.9 ha sow^{-1}, Denmark at 2.0 ha sow^{-1} and Belgium at 2.2 ha sow^{-1} (Teagasc, 2008). 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 (Teagasc, 2008). At 3.5 ha sow^{-1}, the density of pig farming in County Cavan is the densest in the country (Teagasc, 2008).

Landspreading is currently the most cost-effective method of utilizing pig slurry in Ireland (Nolan et al., 2012). Pig slurry is a nutrient-rich fertilizer, with typical values in Ireland taken as 0.8 kg total phosphorus (TP) and 4.2 kg total nitrogen (TN) m^{-3} (The European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2010; hereafter referred to as S.I. No. 610 of 2010). Expressed in terms of cost of chemical fertilisers, these nutrient values would equate to roughly €1.75 and €2.44 m^{-3} for their available TP and TN, respectively, which provides an obvious necessity for farmers to use pig slurry in a strategic manner so as to lessen costs by reducing the requirement for chemical fertilisers. Phosphorus (P; the different forms of P are detailed in Appendix A) losses occur in runoff from two sources: (1) ‘incidental P losses’ take place when a rainfall event occurs shortly after slurry application and before slurry infiltrates the soil, while (2) ‘chronic P losses’ is a long-term loss of P from soil as a result of a build-up in soil test phosphorus (STP) caused by application of inorganic fertilisers and manure (Buda et al., 2009; Schulte et al., 2010). 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). In addition, critical losses of P in runoff can lead to eutrophication of receiving waters (Carpenter et al., 1998). In Ireland, empirical comparison of in-stream phosphate levels and biological quality has demonstrated that once median phosphate concentrations exceed 30 μg P L^{-1}, significant deterioration may be seen in river ecosystems (Clabby et al., 2008).

1.2 Legislation

The EU Water Framework Directive (EU WFD) (European Commission (EC), 2000) aims to achieve ‘at least’ good water quality status in all water bodies of member states by 2015 by implementing a number of Programmes of Measures (POM) in each state. Taking Ireland as an example, S.I. No. 610 of 2010 is Ireland’s POM, which satisfies both the WFD and the Nitrates Directive (EEC, 1991)**.** The Nitrates Directive aims to protect water quality across Europe by preventing nutrients from agricultural sources polluting ground and surface waters by promoting the use of good farming practices. As part of the WFD, all POM implemented must also be a cost-effective means of improving water quality.

Statutory Instrument No. 610 of 2010 (which is due to be reviewed during 2013) puts a limit on the timing, magnitude and placement of inorganic fertilizer and organic manure applications to land. Landspreading of slurry is prohibited during a winter closed period (15th of October to 12-31st of January). Slurry spreading is also prohibited when heavy rainfall is forecast within 48 h of application. This is to allow for increased interaction time between slurry and soil before rainfall, so as to reduce nutrient losses in runoff. Therefore, slurry spreading opportunities may be limited, especially in years with above average rainfall, which can be especially challenging for farmers with insufficient slurry storage capacity. 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 P ha^{-1} yr^{-1}. This limit is dependent on grassland stocking rate and STP (based on plant available Morgan's P (Pm)). Soil P index categories of 1 (deficient) to 4 (excessive) are used to classify STP concentrations in Ireland (Schulte et al., 2010) (Table 1.1).

Table 1.1 Phosphorus index system for Irish grassland (Schulte et al., 2010; Coulter and Lalor, 2008).

Soil P index	Morgan's soil P range (mg L^{-1})	Interpretation
1	0.0–3.0	Soil is P deficient; build-up of soil P required. Insignificant risk of P loss to water.
2	3.1–5.0	Low soil P status: build-up of soil P is required for productive agriculture. Very low risk of P loss to water.
3	5.1–8.0	Target soil P status: only maintenance rates of P required. Low risk of P loss to water
4	>8.0	Excess soil P status: no agronomic response to P applications. Risk of P loss to water increases within this index

The soil P index is based on the Morgan's extraction (Morgan, 1941), with a STP of > 8mg L^{-1} (>10 mg L^{-1} in the case of tillage land) 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). Currently, limits on slurry spreading 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 1.2). As a result, it is estimated that pig farmers will require approximately 50% more spreadlands for manure application in 2017 than was the case in 2012 (Nolan et al., 2012). It may also lead to the need for pig slurry export. Increased chemical fertiliser costs in recent years and farmer changeover from the Rural Environmental Protection Scheme (REPS) to the Agri-Environment Options Scheme (AEOS) has led to increased demand for pig slurry. However, pig slurry export still 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. In order to ensure that P loss is minimised and water quality is improved, supplementary measures are still needed.

Table 1.2 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 1st January 2013, the regulation limits can be exceeded when spreading spent mushroom compost, poultry manure, or pig slurry. 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).

1.3 Water quality in Ireland

1.3.1 Surface water quality

Over 13,000 km of river channel is assessed by the Environmental Protection Agency (EPA) on an ongoing basis at over 2,500 sample points. In the period 2007-2011, approximately 71% of channel length was in an unpolluted condition (EPA, 2012). However, 29% was deemed to be polluted to some degree, with 0.1% classified as being seriously polluted. Diffuse sources were the cause of pollution in roughly half of the sites classified as 'polluted', with agriculture deemed to be the likely cause in 47% of polluted sites (Fig. 1.1). Of 208 lakes and 332 km of canals monitored, 53% and 13%, respectively, were at less than 'good status' (EPA, 2012).

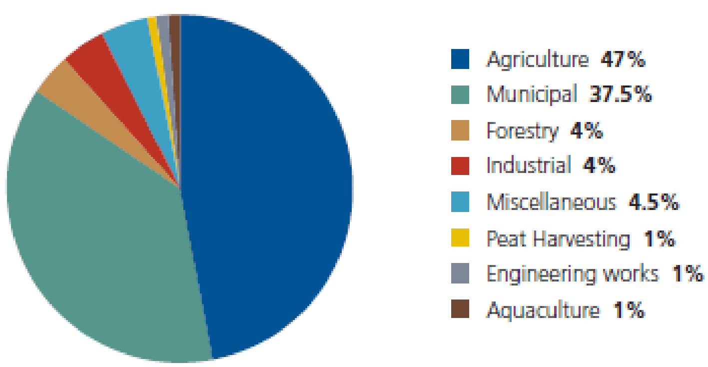

Figure 1.1 Suspected causes of pollution in Irish rivers from the period 2007-2009 (EPA, 2012).

1.3.2 Water quality of groundwater

In the Republic of Ireland, approximately 26% of drinking water supply is taken from groundwater sources, but in some counties (e.g. Co. Roscommon) this figure can be as much as 75% (Lucey, 2009). More than 30% of the annual average flow of water in most rivers in the Republic of Ireland is derived from groundwater (McGarrigle et al., 2010), and in karst limestone areas, groundwater may provide 60 to 80% of the river flow (Lucey et al., 2009). This contribution can increase to greater than 90% during periods of low flow (McGarrigle et al., 2010). Therefore, any change to groundwater quality can have a detrimental effect on river water quality. The EPA found that 15.3% of waterbodies (in over 200 monitoring sites) were classified as being of 'poor status' (EPA, 2012). Although groundwater nitrates (NO_3^-) and P may contribute to nutrient enrichment in receptors such as lakes, rivers and wetlands in vulnerable areas, NO_3^- was the cause of just 0.3% of 'poor' statuses in Ireland compared to 13.3% arising from P, with P concentrations highest in karst aquifers (McGarrigle et al., 2010). Nutrient pressures from agricultural activities (including livestock farming, arable activities and intensive enterprises) and the use of dangerous substances, e.g. agrochemicals, are the most widespread and nationally significant anthropogenic pressure on groundwater quality (McGarrigle et al., 2010).

1.4 Phosphorus mitigation from pig slurry

Whilst pig slurry is almost universally landspread, other options are available. Slurry separation is one alternative. However, this does not treat the slurry; rather, it produces solid and liquid fractions, which are subsequently treated separately.

1.4.1 Slurry separation

Mechanical separation of animal slurry produces an N-rich liquid fraction with a lower dry matter (DM) concentration than the input slurry and a P-rich solid fraction with a higher DM concentration than the input slurry (Gilkinson and Frost, 2007). There are two main types of separator: screen separator and decanting separator. In a screen separator, slurry flows over a metal screen and the liquid fraction passes down through the screen, while the solids are held. Decanting centrifuges use centrifugal forces to increase the settling velocity of suspended particles, causing the heavier solids to move to the outside wall of the cylinder, where they are removed. Transportation costs can be reduced by reducing the water content of slurry, since the volume of pig slurry is the most important factor influencing transportation costs (Nolan et al., 2012). The solid fraction, due to its higher DM and higher P concentration, is cheaper to transport per unit volume of nutrient. This could be transported for application on tillage land, where there is a requirement for plant available P (Nolan et al., 2012). The N-rich liquid fraction can be applied to land in the proximity of the pig farm, where the soil P status is likely to be adequate or in excess of crop requirements. The liquid fraction could also be treated by, for example, constructed wetlands (CWs) or woodchip biofilters, whilst the solid fraction can be treated by composting or used as a feedstock for pyrolysis.

1.4.1.1 Liquid Fraction

1.4.1.1.1 Constructed Wetlands

The use of CWs for the treatment of domestic, municipal (Healy and Cawley, 2002) and agricultural wastewaters (Harrington and McInnes, 2009; Healy et al., 2007) is gaining in popularity, with currently over 140 CWs in existence in Ireland (Babatunde et al., 2008). Constructed wetlands operate in two forms: free water surface (FWS) and subsurface flow (SSF). Free water surface CWs, wherein a shallow layer of wastewater flows over a soil substrate, is the more common design. In SSF CWs, the wastewater flows through a sand or gravel below the surface. Either type of CW may be planted with a mixture of submerged, emergent, and, in the case of FWS CWs, floating vegetation (Healy et al., 2007; Healy and O' Flynn, 2011). Integrated Constructed Wetlands (ICWs) have also become popular in Ireland (Harrington and McInnes, 2009). This is essentially a traditional CW, but is designed with an ecosystem approach that promotes nature conservation and an integrated management of land, water and living resources (Harrington and McInnes, 2009).

The ability of CWs to remove and retain organic matter, sediment and nutrients is dependent on the organic, hydraulic, sediment and nutrient loading rate, media type, vegetation and duration of operation (Healy et al., 2007). Phosphorus can be removed through short-term or long-term storage, with most removal often occurring near the inlet initially, before extending throughout the wetland over time as those sites become P-saturated (Jamieson et al., 2002).

Uptake by bacteria, algae, duckweed and macrophytes provides an initial removal mechanism. However, this is only a short-term P storage, as 35-75% of P stored is eventually released back into the water upon dieback of algae, microbes and plant residues. The only long-term P storage in the wetland is *via* peat accumulation and substrate fixation. The efficiency of long-term peat storage is a function of the loading rate, and also depends on the amount of native iron (Fe), calcium (Ca), aluminium (Al), and organic matter in the substrate.

Harrington and Scholz (2010) investigated the treatment of the separated liquid fraction of anaerobically digested pig manure in meso-scale ICWs and found that ICWs require relatively large footprints in terms of land requirement, and that they were effective in removing total organic N, ammonium (NH_4^+), NO_3^- and molybdate reactive P (MRP) at loading rates of less than 12 g MRP m^{-2} yr^{-1}. However, in Belgium, Meers et al. (2008) reported removal rates of over 99% when treating pig wastewater at loading rates of 64 g TP m^{-2} yr^{-1}. McDowell and Nash (2012) found that the ability of wetlands to remove dissolved P (DP) was much less than their ability to remove particulate P (PP), and that with time, their ability to remove PP decreased. Moreover, in an economic analysis, Nolan et al. (2012) found that the treatment of the separated liquid fraction of pig manure by ICWs, added a cost of €4.60 m^{-3} manure, in addition to separation costs, and was not cost-effective in Ireland in 2012.

1.4.1.1.2 Woodchip biofilters

Woodchip biofilters (Fig 1.2) can be used to treat dilute wastewaters such as dairy soiled water (DSW) or the N-rich, low DM liquid fraction of separated pig slurry. Wastewater passes through the woodchip biofilters and is treated by a combination of physical, chemical and biological processes (Carney et al., 2011). While woodchip filters have been shown to be effective at reducing N concentrations from agricultural wastewaters (Greenan et al., 2009; Robertson et al., 2009; Carney et al., 2011), they do not reduce P concentrations sufficiently to allow release of wastewaters to waterways (Carney et al., 2013).

Figure 1.2 A woodchip biofilter in operation (Carney et al., 2011).

1.4.1.2 Solid Fraction

1.4.1.2.1 Composting

Composting is a natural process by which microorganisms decompose organic matter into simpler compounds and nutrients. Aerobic composting, which takes place in the presence of oxygen, is the quickest way to produce high quality compost (Liang et al., 2003). Composting can only be performed after the pig manure has been separated into its solid and liquid fractions. The process destroys pathogens and weed seeds found in untreated manures, which gives it an advantage over the direct application of untreated manure (Larney and Hao, 2007). It can also reduce its odour and volume, making it cheaper and easier to transport (Bernal et al., 2009). Studies have found that the solid fraction from mechanically-separated pig slurry is too wet to be composted alone and, therefore, requires the use of low-moisture bulking agents (Georgacakis et al., 1996; Nolan et al., 2011), although the addition of bulking agents may lead to an increase in cost. Controlling the temperature, moisture, pH, and oxygen and nutrient conditions during the process is important in ensuring the effectiveness of the composting process.

Composting of the solid fraction of manure has the potential to stabilise the organic N fraction; however, it does not sequester P. Nolan et al. (2012) found that composting the solid fraction of pig manure costs approximately €2.80 m^{-3}, and was not cost-effective compared to landspreading.

1.4.1.2.2 Biochar

The solid fraction of pig manure may be used to produce biochar. Biochar is created by pyrolysis, which is the heating of biomass at high temperatures in the absence of oxygen. During pyrolysis, the organic portion is converted to char and volatile gases. The volatile gases contain condensable tars and incondensable gases, both of which can be burned to produce energy. The tars, when condensed, form combustible pyrolysis oil. The incondensable gases contain a mixture of hydrogen gas (H_2), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen gas (N_2), and hydrocarbon gases (Bridgewater and Peacocke, 2000; Cantrell et al., 2007). The char produced through pyrolysis may also be used as a fuel and can be applied to soil as a soil conditioner, where it has been shown to result in carbon (C) sequestration and altered soil properties, including soil pH, porosity, bulk density, pore-size distribution and water holding capacity (Glaser et al., 2002; Chan et al., 2007; Laird et al, 2010). When char is produced with intent to use as a soil conditioner, it is known as biochar.

There are many advantages of using a thermochemical process such as pyrolysis over common biological treatments (e.g. anaerobic digestion (AD) or composting) for the treatment of animal manures (Cantrell et al., 2007): (1) reactors can be sized to suit the intended application, making them more compact (2) conversion occurs in a matter of minutes (3) pathogens and most pharmaceutically-active compounds are destroyed by the high temperatures (4) the process can use a variety of blended crop residues and animal manure feedstocks (5) the process generates no fugitive gas emissions; and (6) more efficient nutrient recovery is achievable. The effect of amending soil with biochar is dependent on the properties of the specific biochar, including the feedstock and pyrolysis conditions used to produce it (Atkinson et al., 2010), and the properties of the soil (Lehmann and Rondon, 2006). The amendment of soil and landspread pig slurry with biochar has also been shown to reduce nutrient leaching due to its high sorption capacity (Novak et al., 2009; Singh et al., 2010; Troy et al., 2013 a).

The generation of renewable energy through pyrolysis has been shown to result in net reductions in greenhouse gas (GHG) emissions compared to fossil fuel combustion (Gaunt and Lehmann, 2008). However, the net energy generation from the drying and pyrolysis of manure has been shown to be negative due to the high water content (WC) of manures (Ro et al., 2010), creating the need for a bulking agent such as sawdust, which would incur an extra cost, and which can also lead to a reduced yield of biochar (Troy et al., 2013 b).

1.4.2 Anaerobic digestion

Anaerobic digestion is a series of processes in which microorganisms break down biodegradable material, in the absence of oxygen, into a bio-gas, which can be used for both electricity and heat generation. The residue of AD, called digestate, can also be used as a fertiliser. Anaerobic digestion of pig slurry has a number of advantages over landspreading, such as: (1) methane production, which is a renewable fuel that can be used to displace fossil fuels (2) improvement of the fertiliser value due to enhanced nutrient availability and improved flow characteristics (Ward et al., 2008) (3) reduction of pathogens (Massé et al., 2010; Côté et al., 2006) (4) destruction of many weed seeds, reducing the need for herbicides (Frost and Gilkinson, 2010); and (5) reduction in foul odours.

Anaerobic digestors are much more popular in Europe, with approximately 5,900 agricultural biogas plants in operation in the EU in 2010 (Xie et al., 2011). In Germany, more than 4,000 on-farm AD units are in existence (Wilkinson, 2011). The German government intends to increase this number to between 10,000 and 12,000 by 2020 to meet renewable energy targets (Wilkinson, 2011). However, the price available in Germany per kW of electricity produced in AD plants is much more than in Ireland (Blokhina et al., 2011; Nolan et al., 2012). Moreover, AD does not reduce the overall P and N concentration. As pig slurry is generally co-digested with other feedstocks, the N and P content of the digestate may be even higher than that of the raw pig slurry. Therefore, the problem of manure treatment is only replaced with that of digestate treatment. Furthermore, in an economic analysis, Nolan et al. (2012) found that a pig farm-based AD plant in Ireland, co-digesting manure generated by 500 sows with grass silage, would have an annual cost of €54,619 (€5.20 m^{-3} manure) and would not be a financially feasible treatment option.

1.4.3 Buffer strips

Buffer strips and riparian buffer strips (buffer strips beside a water body) are areas of land at the edge of farmland that borders watercourses, maintained in permanent vegetation that intercept P and N loss in runoff. They can also act as a refuge for wildlife, promoting biodiversity. However, they are not effective at preventing losses of DP (McDowell et al., 2004). They work primarily by promoting sedimentation and, therefore, are effective at removing PP, and improving soil structure and infiltration (Lyons et al., 2000). However, there have been mixed results in their performances. McDowell et al. (2004) found that measures such as buffer strips have a limited lifespan and can later serve as a P source. Their effectiveness depends on width, vegetation type and density, soil characteristics (e.g., water infiltration rate and P sorption capacity), placement within the landscape and slope (Fennessy and Cronk, 1997), and it is probably due to this reliance on so many variable factors that their performance has had such mixed results.

1.4.4 Use of P sorbing amendments

1.4.4.1 Amendments applied directly to soil

A potential solution to the possibility of P loss from land-applied pig slurry would be to modify the soil with a P sorbing material. The use of ochre, when mixed to soil in pellet form, may give the soil structure, along with the possibility of the mitigation of chronic P loss, but may give rise to potentially dangerous levels of heavy metals (Fenton et al., 2009). The use of alum or ferric chloride ($FeCl_3$), when mixed with soil, may be advantageous for the mitigation of chronic P losses. Whilst no previous work has been conducted on the application of chemical amendments to soil prior to land application of pig slurry, in a plot study, McFarland et al. (2003) applied dairy wastewater at 20 mm in one dose to three 2.44-m × 3.05-m plots (tested without replication): a control plot, a plot amended with alum (alum dosage, 5.22 kg per plot), and a plot amended with gypsum ($CaSO_4 \cdot 2H_2O$) (gypsum dosage, 5.76 kg per plot). The applied rainfall had an intensity of 76.2 mm h^{-1}, and lasted for 30 min after runoff began. Large decreases in total dissolved phosphorus (TDP) in runoff were observed from the alum-amended plot compared to the control plot, but not in the gypsum-amended plot. The alum-amended plot had a maximum post-application TDP concentration in surface runoff of 0.02 mg L^{-1} compared to a pre-application surface runoff concentration of 0.22 mg L^{-1}. The maximum post-application TDP concentration from the gypsum-amended plot was 0.25 mg L^{-1} compared to a pre-application concentration of 0.18 mg TDP L^{-1}. These compared to the control plot, having a pre-application runoff TDP concentration of 0.13 mg L^{-1} and a maximum post-application of 0.22 mg TDP L^{-1}. Although results are favourable, this method employs a 'double pass' system, whereby a farmer has to travel on land to initially spread the amendment, and then follow a second time to landspread the slurry. This doubles fuel costs and time requirements, and may also lead to increased trafficking and field damage through compaction. In addition, when amendments are spread on land prior to slurry application, they may not adequately mix with slurry, thereby compromising their effectiveness. Any rainfall events in the interim would also lead to amendment being washed away before interacting with slurry.

1.4.4.2 Amendments to slurry

Whilst all of the above mentioned P mitigation measures are effective to a certain degree, all have mitigating characteristics, which, in many cases, is their associated cost. A possible novel alternative is the chemical amendment of pig slurry prior to landspreading. Landspreading is currently the most cost effective treatment option for pig slurry in Ireland (Nolan et al., 2012) and, to date, chemical amendment of pig slurry has never been researched in Ireland. This measure would also improve upon the application of amendment directly to soil so as to more precisely target interaction with the slurry, and also reduce application time and costs. The addition of an amendment to slurry will incur extra costs, and so any recommendations made for the chemical amendment of pig slurry must be mindful of these. Previous research involving dairy cattle slurry (Brennan et al., 2013) has shown the necessity to investigate the occurrence of pollution swapping (the increase in one pollutant as a result of a measure introduced to reduce another pollutant (Healy et al., 2012)), in particular, changes to GHG emissions. It is also possible that soil type may have an impact on the efficacy of amendments.

Chemical amendment of slurry is possible for the control of P, because the negatively charged P, present as orthophosphate (PO_4^{-3}), reacts readily with positively charged Fe^{+3} and aluminum Al^{+3} ions to form relatively insoluble substances.

The reactions are:

$$Al^{+3} + PO_4^{-3} = AlPO_4 \quad [1.1]$$

$$Fe^{+3} + PO_4^{-3} = FePO_4 \quad [1.2]$$

These reactions form the basis for other compounds, such as alum ($Al_2(SO_4)_3.nH_2O$), poly-aluminium chloride ($AlCl_3.6H_2O$) or ferric chloride ($FeCl_3$):

$$Al_2(SO_4)_3.nH_2O + PO_4^{-3} = 2AlPO_4 + 3SO_4^{2-} + nH_2O \quad [1.3]$$

$$AlCl_3.nH_2O + PO_4^{-3} = AlPO_4 + 3Cl^{-} + nH_2O \quad [1.4]$$

$$FeCl_3 + PO_4^{-3} = FePO_4 + 3Cl^{-} \quad [1.5]$$

1.5 Knowledge gaps and project aims

The following knowledge gaps were identified prior to commencing the present study:

1. There has been no research carried out into the effectiveness and feasibility of potential chemical amendments of pig slurry in Ireland to reduce P losses in runoff.

2. Appropriate amendments and suitable rates of addition must be identified within an Irish context.

3. The effectiveness of such amendments on P and metal losses in runoff must be investigated.

4. The effect of chemical amendment of pig slurry on pollution swapping needs to be examined.

5. There is a need to investigate the effects of chemical amendment on P losses in runoff at time intervals between slurry application and rainfall of less than 48 h (currently the

minimum period of time that has to elapse between land application and the occurrence of the first rainfall event (S.I. 610 of 2010)).

6. The effects of soil characteristics, such as buffering capacity, on runoff from chemically-amended slurry must be ascertained.

7. The effect of chemical amendment of pig slurry on STP and soil water extractable P must be assessed.

The hypothesis of this study was that chemical amendment of pig slurry will reduce runoff losses of P, to allow spreading of pig slurry in certain circumstances, and enable WFD targets to be met. Therefore, the objectives of this study were:

1. To select the most appropriate chemical amendments, and their addition rates, to reduce incidental P losses in runoff from pig slurry based on effectiveness, cost and feasibility.

2. To determine the effect of these amendments on suspended sediment, chronic and incidental P and metal losses from land-applied pig slurry.

3. To assess the effectiveness of these amendments at reducing P losses from pig slurry when subjected to rainfall at varying time intervals after land application.

4. To investigate the changes from these chemical amendments on leachate nutrient losses, soil properties and GHG emissions.

5. To identify suitable soil types on which to landspread chemically-amended pig slurry.

1.6 Structure of dissertation

The remainder of the PhD thesis structure is as follows:

Chapter 2 comprises a published paper entitled "Evaluation of amendments to control phosphorus losses in runoff from pig slurry applications to land" (Clean – Soil, Air, Water 40

(2), 164 - 170). This chapter evaluates various chemical amendments, applied at different rates, and identifies the most suitable amendments to add to pig slurry prior to land application. This chapter addresses the first objective of this study.

Chapter 3 comprises a published paper: “Impact of pig slurry amendments on phosphorus, suspended sediment and metal losses in laboratory runoff boxes under simulated rainfall” (Journal of Environmental Management 113, 78 – 84). Selecting the most suitable amendments from Chapter 2, their effect at reducing losses from soil sods following landspreading with amended pig slurry is assessed. This chapter addresses the second objective of this study.

In Chapter 4, the findings of the published paper, “Chemical amendment of pig slurry: control of runoff related risks due to episodic rainfall events up to 48 h after application” (Environmental Science and Pollution Research 20, 6019-6027) are presented. This chapter, which investigates the effectiveness of different amendments at reducing losses from rainfall events at varying intervals up to 48 h following landspreading, addresses the third objective of this study.

In Chapter 5, the findings of the published paper “Impact of chemically amended pig slurry on soil phosphorus, carbon and reactive nitrogen emissions” (Journal of Environmental Management 128, 690-698) are presented. In this chapter, the impacts of using chemically amended pig slurry on leachate nutrient losses, soil properties and GHG emissions are assessed. This chapter addresses the fourth objective of this study.

Chapter 6 assesses which soil types are most suitable to receive chemically amended pig slurry. This chapter, “Changes in soil chemistry following application of chemically amended pig slurry”, has been submitted to Soil Biology and Biochemistry for review, and addresses the fifth objective of this study.

Finally, Chapter 7 details the conclusions and recommendations arising from this research.

1.7 Research Output

Peer reviewed journal papers

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. 40, 164–170. (Appendix B)

O' Flynn, C.J., Fenton, O., Wilson, P., Healy, M.G., 2012. 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. (Appendix C)

O' Flynn, C.J., Healy, M.G., Wilson, P., Hoekstra, N.J., Troy, S.M., Fenton, O., 2013. Chemical amendment of pig slurry: control of runoff related risks due to episodic rainfall events up to 48 h after application. Environ. Sci. Poll. Res. 20, 6019-6027. (Appendix D)

O' Flynn, C.J., Healy, M.G., Lanigan, G.J., Troy, S.M., Somers, C. Fenton, O., 2013. Impact of chemically amended pig slurry on greenhouse gas emissions, soil properties and leachate. J. Environ. Man. 128, 690-698. (Appendix E)

O' Flynn, C.J., Healy, M.G., Wall, D., Fenton, O. Changes in soil chemistry following application of chemically amended pig slurry. Soil. Biol. Biochem. Submitted May 2013.

International/national conference presentations

O' Flynn, C.J., Fenton, O., Wilson, P., Healy, M.G., 2012. Impact of slurry amendments to control phosphorus losses in laboratory runoff boxes under simulated rainfall. 22nd ESAI Colloquium, University College Dublin, 8-10 March, 2012 (Oral presentation).

O' Flynn, C.J., Fenton, O., Wilson, P., Healy, M.G., 2012. Impact of pig slurry amendments to control phosphorus losses in laboratory runoff boxes under simulated rainfall. Agricultural Research Forum. March 12-13. Tullamore, Co. Offaly (Oral presentation).

O’ Flynn, C.J., Fenton, O., Lanigan, G.J., Troy, S.M., Somers, C., Healy, M.G., 2013. Chemical amendment of pig slurry prevents P loss in runoff – but don’t forget to examine gaseous emissions! 23rd ESAI Colloquium, National University of Ireland, Galway. , 30 January-February, 2013 (Oral presentation).

Healy, M.G., Fenton, O., Lanigan, G.J., Grant, J., **O’ Flynn, C.J.**, Brennan, R.B. Slurry amendments reduce incidental P losses but what about N and GHG losses? 15th international RAMIRAN conference, Versailles, France. To be held 3-5 June, 2013 (Poster presentation).

Healy, M.G., Fenton, O., Lanigan, G.J., Grant, J., Brennan, R.B, **O’ Flynn, C.J.**, Serrenho, A. Chemical amendments for the treatment of various types of agricultural effluent. 3rd International conference on pollution and remediation, Toronto, Canada. To be held 15-17 July, 2013 (Oral presentation).

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Chapter 2

Evaluation of amendments to control phosphorus losses in runoff from pig slurry applications to land

Introduction

This chapter identifies the most suitable chemical amendments, and their application rates, to add to pig slurry prior to land application. It has been published in the journal, Clean – Soil, Air, Water (O' Flynn et al., 2012. Evaluation of amendments to control phosphorus losses in runoff from pig slurry applications to land, 40 (2), 164 - 170). Cornelius O' Flynn collected, analyzed, interpreted and synthesized slurry and overlying water data, and is the primary author of this article. Drs. Mark Healy and Owen Fenton contributed to the research design and paper writing.

Evaluation of amendments to control phosphorus losses in runoff from pig slurry applications to land

Cornelius J. O' Flynn[1], Owen Fenton[2], Mark G. Healy [1*]

[1]Civil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of Ireland.
[2]Teagasc, Johnstown Castle, Environmental Research Centre, Co Wexford, Rep. of Ireland

*Corresponding author. Tel: +353 91 495364; fax: +353 91 494507. E-mail address: mark.healy@nuigalway.ie

Abstract

If spread in excess of crop requirements, incidental phosphorus (P) losses from agriculture can lead to eutrophication of receiving waters. The use of amendments in targeted areas may help reduce the possibility of surface runoff of nutrients. The aim of this study was to identify amendments which may be effective in reducing incidental dissolved reactive phosphorus (DRP) losses in surface runoff from land-applied pig slurry. For this purpose, the DRP losses under simulated conditions across the surface of intact grassland soil cores, loaded with unamended and amended slurry at a rate equivalent to 19 kg P ha^{-1}, were determined over a 30-h period. The effectiveness of the amendments at reducing DRP in overlying water were (in decreasing order): alum (86%), flue gas desulphurization by-product (FGD) (74 %), poly-aluminium chloride (PAC) (73%), ferric chloride (71 %), flyash (58%) and lime (54%). Flue gas desulphurization by-product was the most costly of all the treatments (€7.64/m^3 for 74% removal). Ranked from best to worst in terms of feasibility, which takes into account effectiveness, cost and other potential impediments to use, they were: alum, ferric chloride, PAC, flyash, lime and FGD.

2.1 Introduction

The application of slurry in excess of crop requirements can give rise to elevated soil test phosphorus (P) concentrations, which may take years to decades to be reduced to agronomically optimum levels [1]. In addition, it can lead to eutrophication of receiving waters [2]. Phosphorus losses occur in runoff from two sources: (1) 'incidental P losses' take place when a rainfall event occurs shortly after slurry application and before slurry infiltrates the soil, while (2) 'chronic P losses' is a long-term loss of P from soil as a result of a build-up in soil test P caused by application of inorganic fertilisers and manure [1, 3]. The use of amendments may allow the application of manure to soil in intensive farm systems, such as pig farms, while reducing incidental and chronic P losses. This paper proposes a novel and relatively realistic way to identify such amendments.

Alum, aluminium chloride ($AlCl_3$), lime and ferric chloride are commonly used as coagulants in slurry and wastewater separation operations. Smith et al. [4] found in a field-based study that $AlCl_3$, added at 0.75% of final manure volume to pig slurry, could reduce DRP by up to 84%. Smith et al. [5] found that alum and $AlCl_3$, added in a field-based study to pig slurry at 430 mg Al L^{-1}, reduced DRP in runoff water by 84% and DRP in manure by over 99%. In an incubation study, Dou et al. [6] found that technical-grade alum, added to pig slurry at 0.25 kg kg^{-1} of manure dry matter, and flue gas desulpherization by-product (FGD), added at 0.15 kg kg^{-1}, each reduced DRP by 80%. Dao [7] amended stockpiled cattle manure with caliche, alum and flyash in an incubation experiment, and reported water extractable P reductions in amended manure compared to the control of 21, 60 and 85%, respectively.

Batch experiments, wherein an amendment and slurry are mixed, are a good way to determine if the addition of a particular amendment is appropriate to reduce P in surface runoff from land applied slurry, but do not account for the interaction between applied slurry and soil, and the effect of infiltration and skin formation on the release of P to surface runoff. An agitator test, wherein an intact soil core, placed in a beaker, is overlain with continuously-stirred water [8, 9], enables achievement of batch experiment results, but also simulates the situation in which slurry is applied to soil, allowed to dry, and then subjected to overland flow.

The aim of this study was to: (1) investigate the hypothesis that various pig slurry amendments can control incidental P losses in runoff applied to grassland; (2) identify optimum amendment application rates for each amendment; (3) estimate the cost of each treatment; and (4) discuss the feasibility of using amendments in a real on-farm scenario.

2.2 Materials and Methods

2.2.1 Slurry collection and characterisation

Pig slurry was taken from an integrated pig unit in Teagasc Research Centre, Moorepark, Fermoy, Co. Cork. 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 entire sample used for both the batch study and agitator test was taken as one sample. The slurry was stored in a 25 L drum in a cold room at 11^{o}C prior to testing. The total phosphorus (TP) and total nitrogen (TN) were determined using persulfate digestion followed by colorimetric analysis. Ammonium-N (NH_4-N) was determined by adding 50 mL of slurry to 1L of 0.1M HCl, shaking, 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 hr. The physical and chemical characteristics of the pig slurry used in this experiment and some characteristic values of pig slurry from other farms in Ireland and internationally are presented in Table 2.1.

Table 2.1 Physical and chemical characteristics of the pig slurry used in this experiment and characteristic values of pig slurry from other farms in Ireland and internationally.

Location	Total P (mg L^{-1})	Total N (mg L^{-1})	Total K (mg L^{-1})	NH_4-N (mg L^{-1})	pH	Dry matter (%)	Reference
Ireland	560	2150±212		1248 ±40	8.9 ± 0.3	3.5± 0.2	The present study
	800	4200					S.I. No. 610 of 2010
	1630	6621	2666			5.77	18[a]
	900±7	4600±21	2600±10			3.2±2.3	19[a]
Spain	820	3220	1008	1860	7.59	3.2	20
U.S.A.	707	2037	1412	1366		2	21

a) Values changed to mg L^{-1} assuming densities of 1 kg L^{-1}.

2.2.2 Soil preparation and analysis

Grassed soil samples were collected from a local dry stock farm in Athenry, Co. Galway. Aluminium (Al) coring rings, 120-mm-high, 100-mm-diameter were used to collect undisturbed soil core samples (n=60). Soil samples (n=3) – taken from upper 100 mm from the same location - were air dried at 40 °C for 72 hr, crushed to pass a 2 mm sieve and analysed for soil test P using Morgan's extracting solution [10]. 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 [11], and the organic content of the soil was determined using the loss of ignition test [12]. The soil used was a poorly-drained, sandy loam textured topsoil (58% sand, 27% silt, 15% clay) with a soil test P of 16.72±3.58 mg L^{-1}, total potassium of 127.39±14.94 mg L^{-1}, a pH of 7.65±0.06, and an organic matter content of 13±0.1%.

2.2.3 Batch study to determine potential amendments

A batch study was carried out to identify appropriate amendments for the agitator test and the rates at which they should be applied to pig manure to reduce water extractable P, an environmental indicator of potential P loss in slurry. The following amendments were added in the batch study: (1) commercial grade liquid alum (8% Al_2O_3) (2) commercial-grade liquid poly-aluminium chloride (PAC) (10 % Al_2O_3) (3) commercial-grade liquid ferric chloride (38% $FeCl_3$) (4) analytical-grade ferric sulphate ($FeSO_4.7H_2O$) (5) analytical-grade lime ($Ca(OH)_2$) (6) flyash (7) flue gas desulphurization by-product (FGD) (8) bottom ash (9) gypsum (10) aluminium-based water treatment residuals (Al-WTR), sieved to less than 2 mm (Al-WTR-1), and (11) Al-WTR homogenised sludge (Al-WTR-2). Tests 1 – 5 were applied based on a metal:TP stoichiometric ratio and 6 – 11 were applied based on a kg kg^{-1} weight basis (slurry dry matter). The Al-WTR was provided by Galway City Water Treatment Plant. Coal combustion by-products (flyash, FGD and bottom ash) were provided by the Electricity Supply Board. The compositions of all the amendments used are shown in Table 2.2. Values for amendments 1 – 5 are as per manufacturers specifications. The analysis of amendments 6 – 11 was conducted in Teagasc, Johnstown Castle, Co. Wexford.

The pH of the amended slurry was measured after application of amendments at t = 0 h. Amendments were added at 5 different rates to 50 g of slurry and mixed for 10 s. All tests were carried out in triplicate (n=3). At t = 24 h, samples were tested for water extractable P after Kleinman et al. [13]. An unamended sample was also used as a study control.

Table 2.2 Characterisation of amendments used in the batch and agitator tests (mean ± standard deviation) tests carried out in triplicate.

Amendment		Alum	Poly-Al chloride	Ferric Chloride	Ferric Sulphate	Lime	Flyash	FGD	Bottomash	Gypsum	Al-WTR-1	Al-WTR-2
		$Al_2(SO_4)_3.nH_2O$	$AlCl_3.6H_2O$	38% $FeCl_3$	$FeSO_4.7H_2O$	$Ca(OH)_2$					(<2mm)	(sludge)
pH		1.25	1.0 – 3.0				11.2± 0.04	8.6± 0.0			7.9± 0.1	6.9± 0.2
WEP	mg kg^{-1}	0					<0.01	<0.01			<0.01	
Al	%	4.23					5.7± 0.2	0.1± 0.0	0.42	1.1	11± 0.0	5.3± 0.2
Ca						54.1	4.9± 0.2	20± 0.3	0.4	28	1.3± 0.1	0.11
Fe		<0.01		38	20		2.2± 0.1	0.1± 0.0	1.6	0.5	0.2± 0.0	0.01
K							0.1	0.03	0.04	0.01	0.03± 0.0	<0.01
As		1	<1.0	<2.8			13± 0.6	<0.01			6.2±1.1	<0.01
Cd		0.21	<0.2	<3.4			0.6± 0.0	0.2± 0.02	0.28		0.16± 0.0	<0.01
Co							33± 1	0.3± 0.1	0.43		0.5± 0.3	<0.01
Cr		2.1	<2.0	<48			88± 2	3± 0.1	14.3		3.8± 0.21	0.3± 0.02
Cu	mg kg^{-1}			<65			32.7±1.5	37± 13	8.1		31.7± 1.5	0.6± 0.03
Mg							12,200± 610	2,950± 58	2120	12,061	165± 33	3.2± 1.7
Mn				<1370			347± 160	31± 0.6	92		79± 1	6.9± 0.1
Mo							7.7± 0.5	0.73± 0.3	0.63		0.47± 0.2	<0.01
Na							1370± 610	660± 93	859	371	611± 180	65± 14
Ni		1.4	<1.0	<48			44± 1	11± 0.6	9.9		4.8± 0.06	0.6±0.2
P							5460± 630	65± 20	171	218	234± 5.3	18.7± 1.6
Pb		2.8	<2.0	<14			30± 2	0.74± 0.4	3.9		1.2± 0.8	<0.01
V							155± 5	49± 2	13.7		3± 0.2	0.2± 0.01
Zn							75± 31	9.4± 2	19.7		17	0.8± 0.1
Sb			<1.0	<2.8								
Se			<1.0	<2.8								
Hg			<0.2	<0.7								

WEP-water extractable phosphorus; Al-WTR-alum-based water treatment residual; FGD-flue gas desulphurization product.

2.2.4 Agitator Test

The agitator test has been used to investigate the release of P from soil to surface waters [8] and from amended dairy cattle slurry to soil [9]. This experiment replicates the way in which slurry is applied to soil, allowed to dry, and then subjected to overland flow. Although no validation of test results with actual runoff was undertaken, the test provided comparable conditions for assessment of the effectiveness of the amendments at reducing the release of P from land-applied slurry in a realistic way.

In the agitator test, 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 applied at a rate of 19 kg TP ha^{-1} (the control study); (3) grassed sods receiving amended slurry applied at a rate of 19 kg TP ha^{-1}. Six different amendments (selected from the batch study above) were applied at three different rates (low, medium and high; Table 2.3) based on the results obtained from the batch study. Amendments were added to slurry in a 100-mL plastic cup and mixed for 10 s. Prior to the start of the agitator test, the intact soil samples – at approximately field capacity (the water content held in the soil after excess water has drained away) – were taken from their sampling cores and cut to a height of 45 mm; this was considered sufficient to include the full depth of influence on release of soil P to overland flow [8]. They were then transferred into 1-L glass beakers. The slurry and amended slurry was then applied to the soil cores (t = 0 h), and left to interact for 24 h prior to the sample being saturated. At t = 24 h, the samples were gently saturated by adding deionised water to the soil at intermittent time intervals over 24 h until water pooled on the surface. Immediately after saturation (t = 48 h), 500 mL of deionised water was added to the beaker. The agitator paddle was lowered to mid-depth in the water overlying the soil sample and the paddle was set to rotate at 20 rpm for 30 h to simulate overland flow (Fig. 2.1). Water samples (4 ml) were taken from mid-depth of the water overlying the soil at 0.25, 0.5, 1, 2, 4, 8, 12, 24 and 30 h after the start of each test (i.e. after the 500 ml was added). All samples were filtered immediately after sample collection using 0.45-μm filters and prior to being analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Readings for pH were taken in the overlying water at 1 h and 30 h after the start of each test. The agitator experiment was sufficient to compare treatments, but concentrations do not represent actual values at field scale.

Figure 2.1 The agitator experimental setup.

2.2.5 Cost

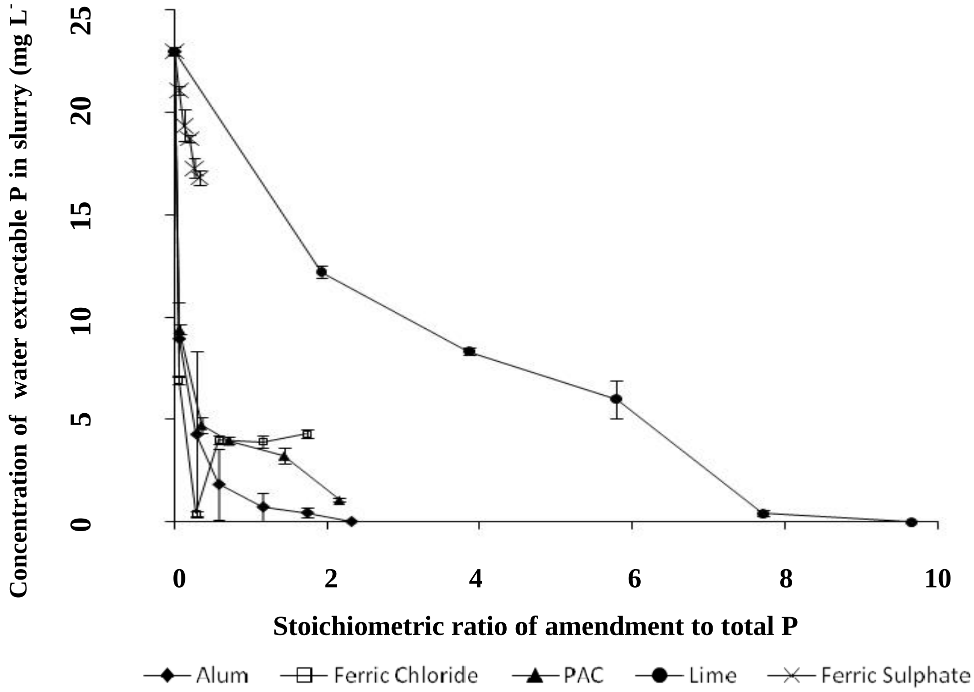
The effects of amendments on slurry viscosity or handling were not considered in the cost analysis. It was assumed that amendments would be added upon delivery, so storage cost on site was excluded from the analyses. In the case of lime, the cost was estimated using commercial grade lime. The calculated costs took into account the fixed and operational costs for a 75 kW tractor and 2000 gal. splash-plate slurry tanker.

2.3 Results

2.3.1 Batch study

The most effective amendments at reducing water extractable P after 24 h were (in decreasing order of effectiveness): alum (99%), lime (99%), ferric chloride (98%), PAC (95%), flyash (87%), FGD (76%), gypsum (39%), ferric sulphate (27%), bottom ash (24%), Al-WTR-2 (15%) and Al-WTR-1 (0%) (Fig. 2.2).

a)



b)

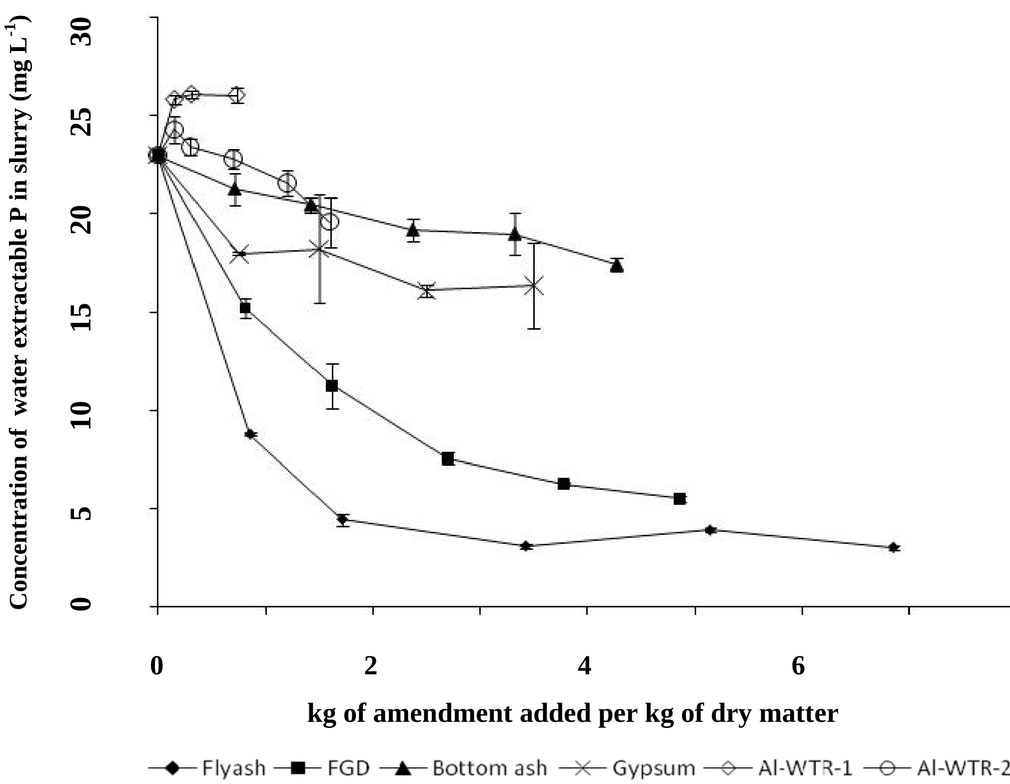


Figure 2.2 Concentration of water extractable P (± standard deviation) in pig slurry (mg L^{-1}) as a function of stoichiometric ratio of Al added as alum and poly-Al chloride (PAC); Fe added as ferric chloride and ferric sulphate; and Ca as lime to total P in pig slurry (a), and mass of flyash, flue gas desulphurization by-product (FGD), bottom ash, gypsum, and Al-based water treatment residuals sieved to less than 2 mm (Al-WTR-1) and homogenized sludge (Al-WTR-2) added per dry matter of pig slurry (b).

For all solutions, there was a point beyond which further additions of amendments did not significantly reduce water extractable P (Fig. 2.2). On the basis of inspection of the results, the amendments and their application rates to be used in the agitator test were: (1) alum (0.29:1, 0.58:1, 0.88:1 [Al:P]); (2) PAC (0.18:1, 0.36:1, 0.72:1 [Al:P]); (3) ferric chloride (0.34:1, 0.62:1, 0.89:1 [Fe:P]); (4) lime (3.86:1, 5.79:1, 7.79:1 [Ca:P]); (5) flyash (0.857, 1.71, 3.43 kg kg^{-1} DM); and (6) FGD (2.7, 3.78, 4.86 kg kg^{-1} DM).

2.3.2 Agitator test

Figure 2.3 shows the mass of DRP in the overlying water and DRP concentrations over the study duration. The percentage reduction in DRP for each treatment at each rate is shown in Table 2.3. The unamended slurry had a DRP concentration of 17.8 mg L^{-1} in the overlying water. The DRP concentrations in the overlying water, ranked from best to worst, were: alum, 2.5 mg L^{-1}; FGD, 4.6 mg L^{-1}; PAC, 4.7 mg L^{-1}; ferric chloride, 5.2 mg L^{-1}; flyash, 7.5 mg L^{-1}; and lime, 8.1 mg L^{-1}. These compare to the water overlying the grassed sod-only treatment, which had a DRP concentration of 2.0 mg L^{-1}.

2.3.3 Cost

Table 2.3 shows the estimated cost of addition of amendments and estimations of spreading and agitation costs as a result of their use. In order of increasing cost of use, per m^3 of pig slurry, they are: ferric chloride (€1.89); flyash (€2.00); PAC (€2.09); alum (€2.18); lime (€2.84) and FGD (€4.10). Figure 2.4 shows the total cost of amendment (€ $tonne^{-1}$) versus percentage reduction in DRP release to overlying water (%) and the reduction in DRP released from soil (kg ha^{-1}). The addition of FGD led to dry matter contents of above 10%, which would require water to be added to produce dry matter of a low enough consistency for slurry spreading operations. Addition of water would require agitation and these, combined with the high volume of addition per m^3, significantly increased the total cost of FGD above the other amendments. Alum, although clearly the best performing amendment, was still competitively priced compared to the other amendments.

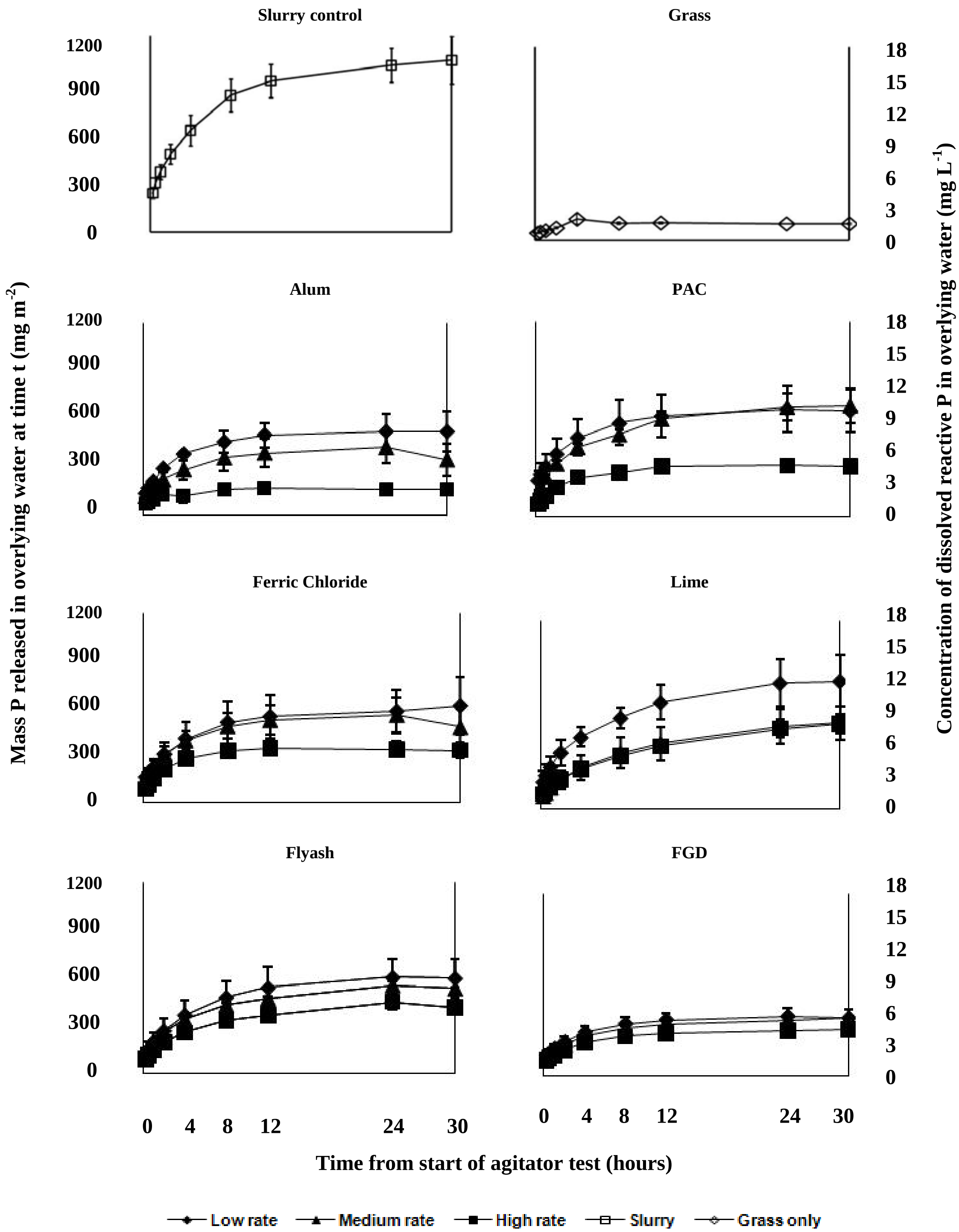


Figure 2.3 The mass of dissolved reactive P (DRP) (mg m^{-2}) and DRP concentration (mg L^{-1}) in water overlying grassed sod-only treatment; grassed sod with unamended slurry; and grassed sod with slurry amended with alum, poly-Al chloride (PAC), ferric chloride, lime, flyash and flue gas desulphurization by-product (FGD), each applied at three different rates, plotted over the 30 h of the test.

Table 2.3 Table showing amendments in order of feasibility score, breakdown of costs[a], cost/m^3 slurry[b], cost for 500 sow integrated unit, percentage reduction in DRP in overlying water at 30 h.

Amendment[c]	Feasibility score	Addition rate[d]	Cost[e]	Rate	Cost of amendment	Spreading	Agitation	Cost water[f]	Total	500 sow integrated unit[g]	DRP Removal	Extra cost per unit DRP reduced in runoff	Spreading rate of metal	Within max allowable metal spreading rates[h]
			€/tonne	kg/m^3	€/m^3	€/m^3	€/m^3	€/m^3	€/m^3	€/farm	%	€/kg DRP/ha	kg/ha	Yes/No
Control					0.00	1.56	0.00	0.00	1.56	16,182	0	0		
Alum	1	0.29:1 Al: P	150	4	0.58	1.60	0.00	0.00	2.18	22,672	55	1.71	5.51	No limit
		0.58:1 Al: P		8	1.16	1.56	0.00	0.00	2.72	28,309	64	2.78	11.02	
		0.88:1 Al: P		12	1.76	1.57	0.00	0.00	3.33	34,613	86	3.14	16.72	
Ferric Chloride	2	0.34:1 Fe: P	250	1	0.34	1.55	0.00	0.00	1.89	19,704	48	1.08	6.46	No limit
		0.62:1 Fe: P		2	0.62	1.55	0.00	0.00	2.18	22,655	52	1.81	11.78	
		0.89:1 Fe: P		4	0.90	1.56	0.00	0.00	2.45	25,500	71	1.92	16.91	
Poly-Al chloride	3	0.18:1 Al: P	280	2	0.53	1.55	0.00	0.00	2.09	21,689	43	1.85	3.42	No limit
		0.36:1 Al: P		4	1.07	1.56	0.00	0.00	2.62	27,258	42	3.86	6.84	
		0.72:1 Al: P		8	2.13	1.56	0.00	0.00	3.69	38,396	73	4.42	13.68	
Flyash	4	0.030 kg/kg	14	30	0.40	1.60	0.00	0.00	2.00	20,815	43	1.58		Yes
		0.060 kg/kg		60	0.81	1.64	0.00	0.00	2.45	25,488	48	2.85		
		0.120 kg/kg		120	1.62	1.74	0.00	0.00	3.36	34,910	58	4.75		
$Ca(OH)_2$	5	3.86:1 Ca: P	312	4	1.28	1.56	0.00	0.00	2.84	29,511	30	6.41	73.34	No limit
(Lime)		5.79:1 Ca: P		6	1.92	1.56	0.00	0.00	3.48	36,206	53	5.48	110.01	
		7.71:1 Ca: P		8	2.56	1.56	0.00	0.00	4.12	42,866	54	7.25	146.49	
FGD	6	0.095 kg/kg	14	95	1.28	1.98	0.43	0.42	4.10	42,634	66	5.80		Yes
		0.132 kg/kg		132	1.79	2.49	0.54	1.09	5.91	61,467	67	9.82		
		0.170 kg/kg		170	2.30	2.98	0.64	1.73	7.64	79,474	74	12.52		

DRP-dissolved reactive P; FGD-flue gas desulphurization product; a) Calculations based on an integrated pig unit with 500 sows, or equivalent stocking rate, indoors for 52 weeks; b) Slurry properties: Total P = 560 mg L^{-1} and 3.5% dry matter (DM); c) In the case of $Ca(OH)_2$, cost was estimated using commercial grade lime; d) Addition rates for Flyash and FGD quoted as kg of ammendment/kg of slurry; e) Cost includes delivery of material and addition of material to slurry in storage tank; f) Addition of some amendments resulted in DM >10%-water addition needed for spreading. In this case, agitation is required for process of adding water; g) Calculations based on 0.4 m^3 of slurry/sow/week; h) Max allowable metal application rates take from S.I. No. 267/2001-Waste Management (Use of Sewage sludge in Agriculture) (Amendment) Regulations, 2001 (www.irishstatutebook.ie).

2.4 Discussion

In the batch study, Al-WTR-1 and Al-WTR-2 increased the water extractable P of the slurry when added at some weights. This may be attributable to the fact that there were small quantities of P within Al-WTR-1 and Al-WTR-2 (Table 2.2). There was also P present in flyash and FGD, but these amendments contained much more calcium (Ca) and magnesium (Mg), which are P sorbing elements. Lime required a much higher stoichiometric addition rate to achieve significant water extractable P reduction; however, this is acceptable as lime is often added to land by farmers and has widespread public acceptance. Ferric sulphate was not tested above a stoichiometric rate of 0.332, as there was a poor response relative to the other amendments at the same addition rate. The reduction in water extractable P compared favourably to that of Dao et al. [7], who reported reductions of 60% and 85% in water extractable P concentrations after adding alum and flyash, respectively, to stockpiled cattle manure.

Taking into account costs, land application of metals and potential DRP reductions in overlying water, the amendments, ranked in decreasing order of feasibility, were: alum, ferric chloride, PAC, flyash, lime and FGD.

There was a high initial rise in DRP at the start of each test, with the rate of increase reducing over time towards the end of the study (Fig. 2.3). It can be seen in almost all cases that the higher the addition rate for each amendment, the lower the peak in DRP concentration. The amendments used in the agitator test all reduced the DRP concentrations in the overlying water. However, they did not reduce the concentrations to below that of the grassed sod-only treatment, which itself was well above 30 $\mu g\ P\ L^{-1}$, the median phosphate level above which significant deterioration may be seen in river ecosystems [14]. The reason for this is the amendments only reduce the contribution of the slurry to the overlying water DRP, and do not affect the contribution of the soil to the overlying water DRP. The reductions in DRP were broadly similar to those of Smith et al. [5], who achieved reductions in DRP of 84% in runoff water when adding both alum and $AlCl_3$ to pig slurry at 430 mg Al L^{-1} in a field-based study.

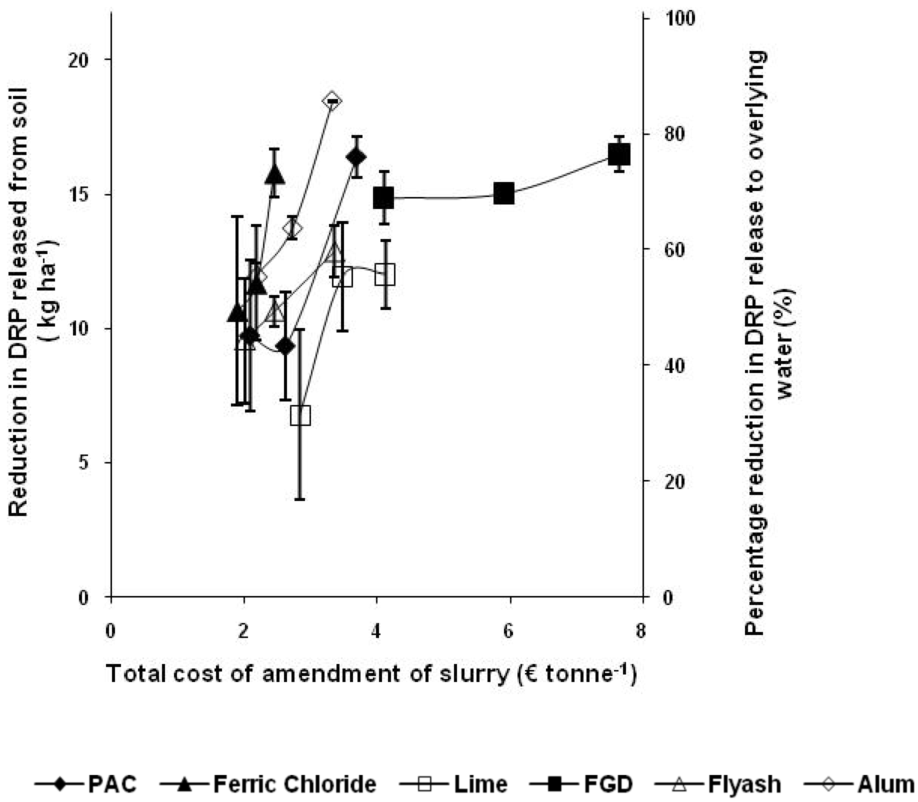


Figure 2.4 Total cost of amendment (€ tonne^{-1}) of pig slurry plotted against the reduction in dissolved reactive P (DRP) lost to overlying water (kg ha^{-1}) and the percentage reduction in DRP release to overlying water from slurry amended with alum, poly-Al chloride (PAC), ferric chloride, lime, flyash and flue gas desulphurization by-product (FGD), each applied at three different rates.

The effect of amendments on slurry pH is a potential barrier to their implementation, as it affects P sorbing ability [15] and ammonia (NH_3) emissions from slurry [16]. The use of acidifying amendments can lead to increased release of hydrogen sulphide gas (H_2S) from slurry, which is believed to be responsible for human and animal deaths when slurry is being agitated on farms. However, the results from this experiment show the pH of the overlying water not to be significantly affected by the use of amendment.

From the cost analysis, it can be seen that the use of amendments may only be worth pursuing where focused application may be adopted. As legislation allows less slurry to be spread on high P index soils, farmers with these soils have less land available on which to spread slurry. The addition of amendment to pig slurry has the potential to relieve this problem. If a farmer has more than one P index level on a farm, then a way to potentially reduce the cost associated with amending the slurry would be to only amend the slurry that is applied to areas of the farm with a higher soil test P. However, this will only reduce the impact of landspreading on the potential loss of P in runoff and will not impact on the soil test P, which will still be a potential pollution source.

Although this study did not investigate the release of metals due to the amendment of slurry, previous studies that have found no added risk was posed by amending land applied pig [4] or poultry [17] manure. Moore et al. [17] also investigated whether using alum as an amendment affected Al concentrations in the soil or Al uptake by plants. They showed that use of alum did not negatively affect either. The reason that Al availability was not affected is because Al availability in soils is virtually independent of the level of total Al, but instead is controlled by the geochemical conditions present, with pH being the major influencing factor. Acidic conditions result in the dissolution of clay minerals and Al oxides, causing high concentrations of exchangeable Al. The soil's pH would be expected to increase, resulting in decreased available Al. Moore et al. [17] also calculated that it would take 400 years of annual application of alum-treated litter to increase the level of total Al in the soil from 7 to 8%, with alum already being the most abundant metal in most soils. However, available Al would still theoretically decrease.

2.5 Conclusions

The findings of this study are:

1. All of the amendments trialled in the agitator test have the potential to reduce the release of P in surface runoff from land-applied slurry.
2. Taking into account costs and land application of metals, suitable amendments which may reduce the risk of surface runoff of P from land applied pig slurry are (in decreasing order of feasibility): alum, ferric chloride, PAC, flyash, lime and FGD.
3. As there are significant costs associated with the use of these amendments, it is recommended that they are used strategically in areas which are likely to have potential nutrient loss problems. As land surrounding pig farms tend to have high soil test phosphorus, the use of amendments may be deemed necessary. Although they

reduce the impact of nutrient loss from land application of pig slurry, they do not prevent the loss of nutrients from soil of high nutrient content.

2.6 Acknowledgements

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Summary

This chapter showed that the amendments examined in the agitator test have the potential to reduce the release of P in surface runoff from land-applied slurry. The next chapter focuses on the removal of P in a more realistic setting, with slurry and amended slurry subjected to actual runoff at a more representative scale.

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Chapter 3

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

Introduction

This chapter evaluates the effect of chemical amendment of pig slurry, prior to application on soil sods, on runoff losses. It has been published in the Journal of Environmental Management (O' Flynn et al., 2012. Impact of pig slurry amendments on phosphorus, suspended sediment and metal losses in laboratory runoff boxes under simulated rainfall, 113, 78 - 84). Cornelius O' Flynn collected, analysed and interpreted slurry, soil and runoff water experimental data, and is the primary author of this article. Drs. Mark Healy and Owen Fenton contributed to the research design and paper writing. Dr. Paul Wilson conducted the statistical analysis.

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

C.J. O' Flynn[a], O. Fenton[b], P. Wilson[c,d], M.G. Healy [a*]

[a]Civil Engineering, National University of Ireland, Galway, Co. Galway, Ireland.
[b]Teagasc, Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland
[c]School of Mathematics and Statistics, University of St. Andrews, Fife, Scotland
[d]School of Mathematics, Statistics and Applied Mathematics, National University of Ireland, Galway, Co. Galway, Ireland.

*Corresponding author. Tel: +353 91 495364; fax: +353 91 494507. E-mail address: mark.healy@nuigalway.ie

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.

3.1 Introduction

The European Union Water Framework Directive (WFD) (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 S.I. No. 610 of 2010) is Ireland's POM, which satisfies both the WFD and the Nitrates Directive (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 3.1). 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 slurry 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.

Table 3.1 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).

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, not explored by Nolan et al. (2012), is the chemical amendment of pig slurry. Based on a laboratory scale experiment, it was suggested in Chapter 2 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 desulfurization 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.

Chapter 2 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 were 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 SS losses during three consecutive simulated rainfall events and to:

1) Elucidate if amendment of pig slurry controls 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.

3.2 Materials and Methods

3.2.1 Slurry collection and characterisation

Pig slurry was taken from an integrated pig unit in Teagasc Research Centre, Moorepark, Fermoy, Co. Cork, Republic of Ireland 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^{o}C prior to testing. The TP and total nitrogen (TN) were determined using persulphate digestion. Ammonium N (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 Whatman No. 2 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 3.2.

Table 3.2 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

3.2.2 Soil collection and analysis

Intact grassed soil samples (n=15), 120-cm long, 30-cm wide, 10-cm deep, were collected from a local dry stock farm in Galway, Republic of Ireland. Soil samples (n=3) – taken from the upper 10 cm 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 (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 3.1), 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%.

3.2.3 Slurry amendment

The results of a laboratory micro-scale study in Chapter 2 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 Chapter 2 (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 3.3.

3.2.4 Rainfall simulation study

Stainless steel laboratory runoff boxes, 100 cm-long, 22.5 cm-wide and 7.5 cm-deep 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 (Fig. 3.1) 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, 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 (Fig. 3.2, 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 (the water content held in the soil after excess water has drained away), 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.

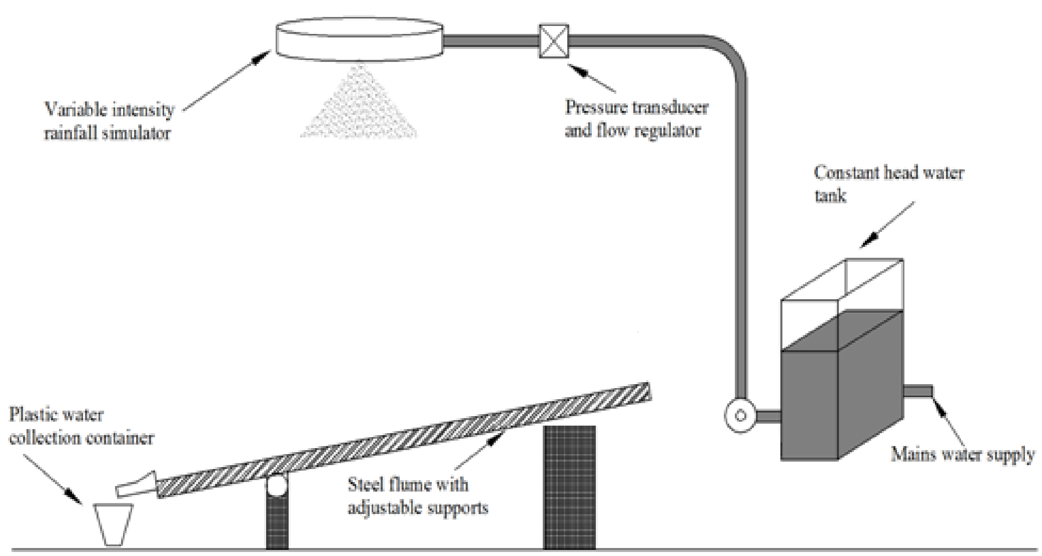

Figure 3.1 The rainfall simulator experimental setup.

3.2.5 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 0.45-µm filter and analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Filtered (passed through a 0.45-µm filter) and unfiltered subsamples, collected at 10, 20 and 30 min after runoff began, were tested for total dissolved P (TDP) and TP using acid persulphate digestion. Particulate phosphorus was calculated by subtracting TDP from TP. Dissolved un-reactive phosphorus (DUP) 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}.

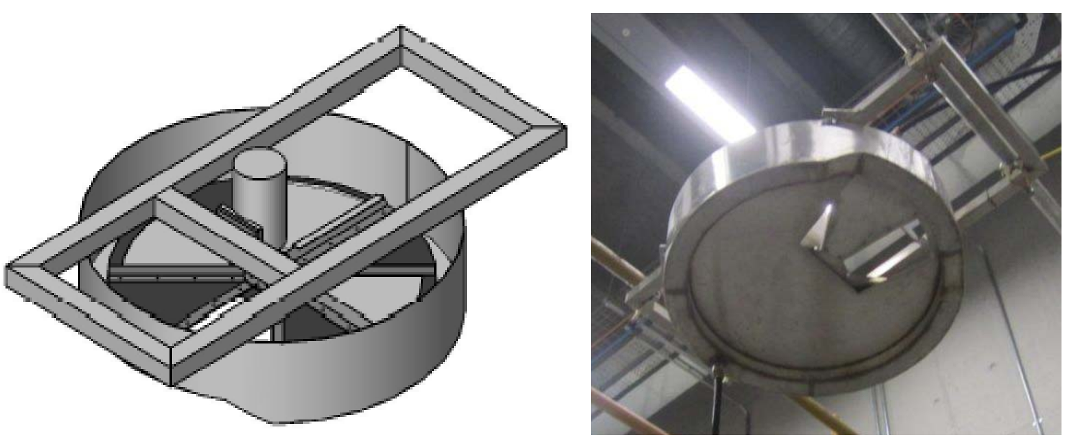

Figure 3.2 Rainfall Simulator (isometric drawing and photo of underside).

Table 3.3 Characterisation of amendments used in this study.

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	mg kg^{-1}	0.21	<3.4	<0.2
Co	mg kg^{-1}			
Cr	mg kg^{-1}	2.1	<48	<2.0
Cu	mg kg^{-1}		<65	
Mg	mg kg^{-1}			
Mn	mg kg^{-1}		<1370	
Mo	mg kg^{-1}			
Na	mg kg^{-1}			
Ni	mg kg^{-1}	1.4	<48	<1.0
P	mg kg^{-1}			
Pb	mg kg^{-1}	2.8	<14	<2.0
V	mg kg^{-1}			
Zn	mg kg^{-1}			
Sb	mg kg^{-1}		<2.8	<1.0
Se	mg kg^{-1}		<2.8	<1.0
Hg	mg kg^{-1}		<0.7	<0.2

3.2.6 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.

3.3 Results and Discussion

3.3.1 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 neighbouring such a landscape. The high drainage density, high annual rainfall and low annual potential evapotranspiration (20–50% of rainfall) facilitate 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 by the landscape before reaching an 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. 3.3). 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. 3.3). 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 3.4). Although the concentration of TDP in runoff from the slurry control decreased slightly during each event (Fig. 3.3), 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 relatively 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 3.4); 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.

Table 3.4 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 ($p < 0.05$)

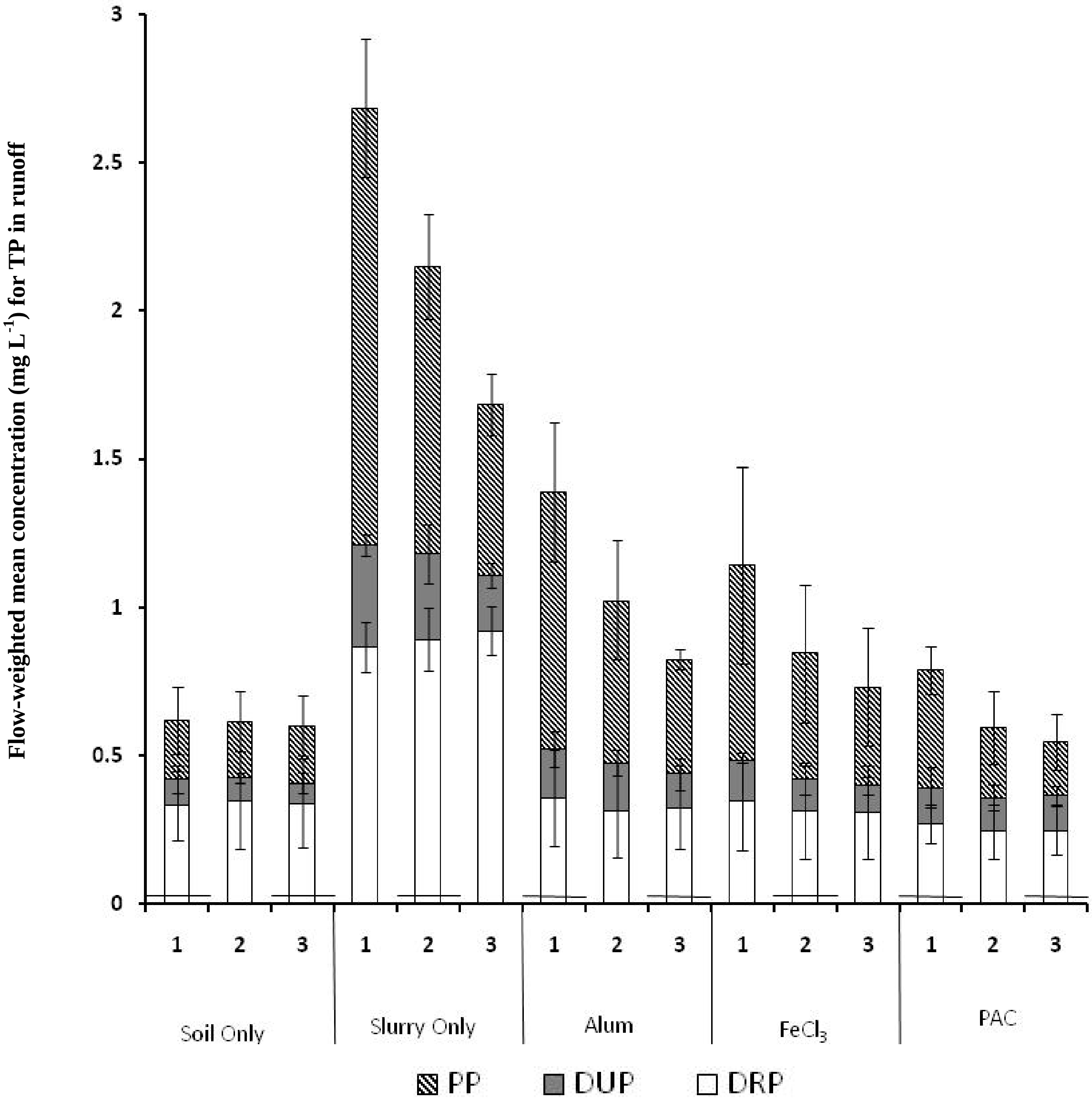

Figure 3.3 Histogram of flow-weighted mean concentrations (mg L^{-1}) for dissolved reactive phosphorus (DRP), dissolved unreactive phosphorus (DUP) and particulate phosphorus (PP) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry. Hatched line = 30 µg P L^{-1} standard (Clabby et al., 2008).

The average FWMC of DRP and TDP in runoff from the amended slurry treatments were approximately half of that 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 3.4).

3.3.2 Suspended sediment, metals and pH in runoff

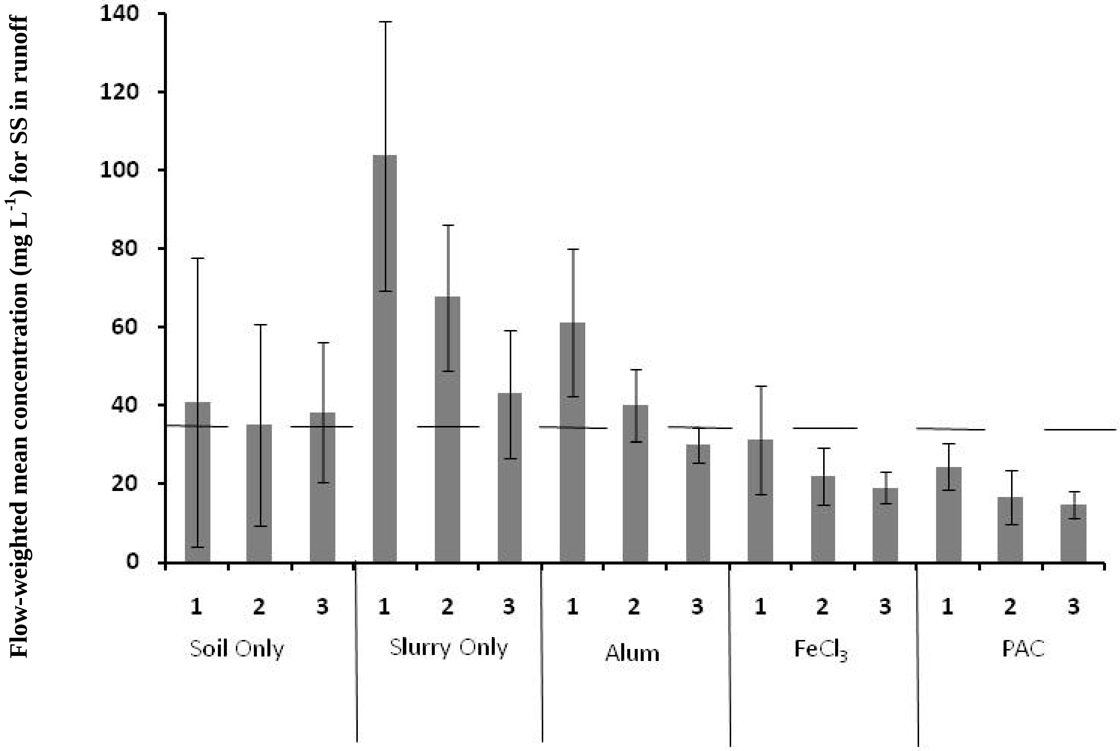

Figure 3.4 Histogram of average flow-weighted mean concentration of suspended sediment (SS) (mg L^{-1}) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry. Hatched line = 35 mg L^{-1} standard (S.I. No 419 of 1994).

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. 3.4) 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.

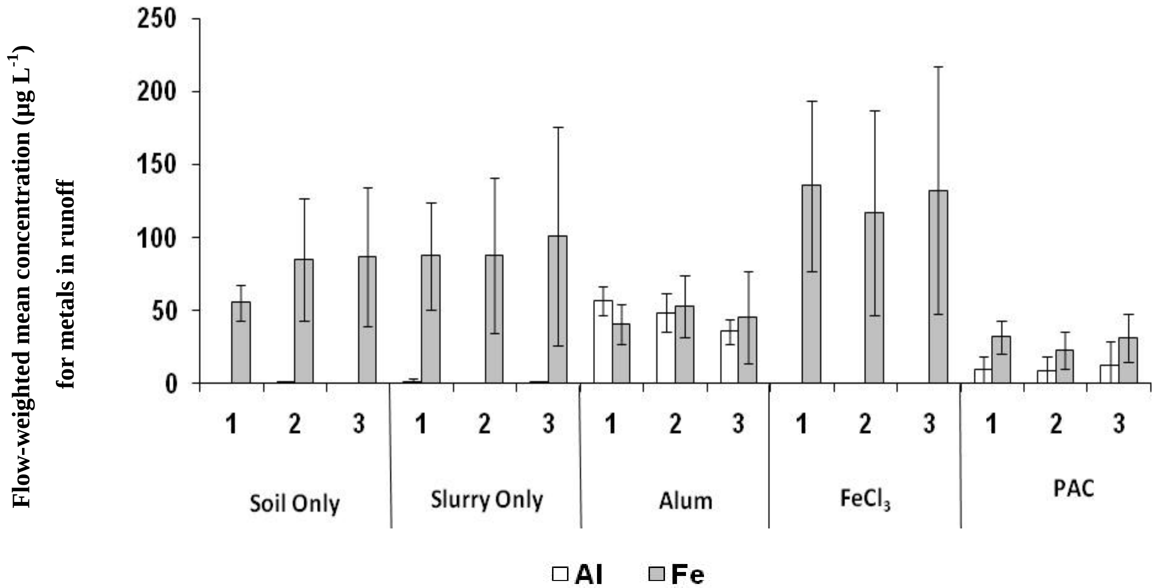

Figure 3.5 Histogram of average flow-weighted mean concentration of metals (mg L^{-1}) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry.

Figure 3.5 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). Ferric chloride 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 mg L^{-1} 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.

3.3.3 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. In Chapter 2, it was 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, not examined in the present study, would be to modify the soil with a P sorbing material.

3.4 Conclusions

The findings of this study were:

1. On the high STP soil tested, P losses from the grassed soil-only were high and were further increased following slurry application. All amendments tested reduced all types of P losses, but did not reduce them significantly to below that of the soil-only treatment, the average FWMC of TP of which was 0.61 mg L^{-1} and which comprised 31% as PP. For the slurry control, the average FWMC of the surface runoff was 2.17 mg TP L^{-1}, 47% of which was PP. In decreasing order of effectiveness at removal of P, the most successful amendments were: PAC, which reduced the average FWMC of TP to 0.64 mg L^{-1} (42% PP); $FeCl_3$, which reduced TP to 0.91 mg L^{-1} (52% PP); and alum, which reduced TP to 1.08 mg L^{-1} (56% PP).
2. For each treatment, TP and TDP concentrations in runoff decreased after each RE. However, the fraction of TDP within runoff increased, due to large, although not significant, decreases in PP between events.
3. The amendments all reduced the SS to below that of the slurry control, and in the case of $FeCl_3$ and PAC, to below that of the soil only. These two treatments also reduced the average FWMC of SS 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.

3.5 Acknowledgements

The first author gratefully acknowledges the award of the EMBARK scholarship from IRCSET to support this study. The authors would like to thank Raymond Brennan and Liam Henry.

Summary

This chapter showed that chemical amendment of pig slurry led to decreased losses of P and SS in runoff at events 48 h and more after application. The next chapter will investigate the effect of amendments during rainfall at time intervals between application and rainfall of less than 48 h, to see if chemical amendment can make slurry spreading operations more flexible for farmers.

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Chapter 4

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

Introduction

This chapter examines the effect of chemical amendments on runoff losses from rainfall events at varying intervals up to 48 h following landspreading, and has been published in Environmental Science and Pollution Research (O' Flynn et al., 2013. Chemical amendment of pig slurry: control of runoff related risks due to episodic rainfall events up to 48 h after application, 20, 6019-6027). Cornelius O' Flynn collected analysed and interpreted slurry, soil and runoff water data, and is the primary author of this article. Drs. Mark Healy, Owen Fenton, Nyncke Hoekstra and Shane Troy contributed to the research design and paper writing. Dr. Paul Wilson conducted the statistical analysis.

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

Cornelius J. O' Flynn[a], Mark G. Healy [a*], Paul Wilson[c], Nyncke J. Hoekstra[b], Shane M. Troy[d], Owen Fenton[b]

[a]Civil Engineering, National University of Ireland, Galway, County Galway, Ireland.
[b]Teagasc, Environmental Research Centre, Johnstown Castle, County Wexford, Ireland.
[c]School of Technology, University of Wolverhampton, Wolverhampton, UK.
[d]Scottish Rural College, Roslin Institute Building, Edinburgh, UK.

*Corresponding author. Tel: +353 91 495364; fax: +353 91 494507. E-mail address: mark.healy@nuigalway.ie

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 water body by prohibiting slurry spreading when heavy rainfall is forecast within 48 h. 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 48 h) between pig slurry application and simulated rainfall with an intensity of 11.0±0.59 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% 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 (10 % Al_2O_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 48 h 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 12 h were less than from unamended slurry with a TI of 48 h, 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

4.1 Introduction

During episodic rainfall events, phosphorus (P) and reactive nitrogen (N_r) fluxes from critical (soil) and incidental (e.g. slurry or fertiliser 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; Monteney 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 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 48 h 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 48 h, which is the limit set by Irish and UK regulations. Assessing the risk of runoff at TIs within these 48 h 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 48-h limit does not unnecessarily restrict the opportunity of farmers to apply slurry. To the best of our knowledge, there are no studies that address the validity of adhering to a 48-h 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 48 h 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 48 h 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 ($AlCl_3$), lime and ferric chloride ($FeCl_3$) 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; Chapter 2; Chapter 3). In particular, Chapter 3 showed that the runoff losses from amended pig slurry 48 h 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 48 h between application and first rainfall event.

Therefore, the aim of this study was to investigate the effect of TI (12, 24 and 48 h) between pig slurry application and first rainfall event on the losses of P and suspended solids (SS) in runoff, and to assess the hypothesis that adding chemical amendments may be more effective than current TI-based legislation.

4.2 Materials and Methods

4.2.1 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^{o}C prior to testing. Total P (TP) and total nitrogen (TN) were determined using persulfate digestion. Ammonium-N (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^{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 4.1.

Table 4.1 Physical and chemical characteristics[a] 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})				(%)	
482±37	3,850±20		2250 ±72	7.37 ± 0.07	3.22± 0.15	The present study
800	4,200					S.I. No. 610 of 2010
1630	6,621	2,666			5.77	McCutcheon 1997[b]
900±7	4,600±21	2,600±10			3.2±2.3	O' Bric 1991[b]

[a]TP total P; TN total N; TK total K; DM dry matter. [b]Values changed to mg L^{-1} assuming densities of 1 kg L^{-1}.

4.2.2 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 4.2) as determined in Chapters 2 and 3. 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 poly-aluminium chloride (PAC) (10%

Al_2O_3) applied at a rate of 0.72:1 [Al/TP]. The compositions of the amendments used are the same as those used in Chapters 2 and 3.

4.2.3 Soil collection and analysis

Intact grassed soil samples 120 cm-long, 30 cm-wide, 10 cm-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 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 Standards Institution 1990a) and the organic content of the soil was determined using the loss on ignition test (British Standards Institution 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^{-1}, 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 of 203 mg L^{-1}, a pH of 6.4±0.3 and an organic matter content of 5±2%.

4.2.4 Rainfall simulation study

The following treatments were examined within 21 days 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}. 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 48 h (TI 3).

Table 4.2 Flow-weighted mean concentrations (mg L^{-1}) averaged over three time intervals, application costs per tonne, metal application rate (kg ha^{-1}), and removals (%) for dissolved reactive P (DRP), dissolved un-reactive P (DUP), total dissolved P (TDP), particulate P (PP), total P (TP) and suspended solids (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 %	Costs € $tonne^{-1}$	Metals kg ha^{-1}
Soil Only	0.10a	-	0.11a	-	0.21a	-	0.14a	-	0.35a	-	15.98a	-	-	-
Slurry Only	1.34b	-	0.60c	-	1.94c	-	3.85c	-	5.78c	-	377.60c	-	-	-
Alum	0.21a	84	0.28b	53	0.49b	74	1.78b	54	2.27b	61	101.30b	73	150	16.72[a]
$FeCl_3$	0.21a	84	0.19b	69	0.40b	80	1.48b	61	1.88b	67	139.94b	63	250	16.91[b]
PAC	0.22a	84	0.26b	56	0.48b	75	2.01b	48	2.49b	57	135.68b	64	280	13.68[a]

Means in a column, which do not share a letter, were significantly different ($p < 0.05$). [a]Spreading rate of Al. [b]Spreading rate of Fe.

Stainless steel laboratory runoff boxes, 1 m-long, 0.225 m-wide and 0.075 m-deep, with side walls of 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, USA) attached to a 4.5 m high metal frame, and calibrated to achieve an intensity of 11.0±0.59 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 dissolved reactive P (DRP) concentration of less than 0.005 mg L^{-1}, a pH of 7.7±0.2 and an electrical conductivity of 0.44 dS m^{-1}. 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 24 h 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 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 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-µm filter and analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Filtered (passed through a 0.45-µm 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 unreactive 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 μm) filter paper. Prior to filtration, the filter paper was weighed. After filtration, the filter paper was dried at 105^{o}C for 24 h and reweighed.

4.2.5 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 $FeCl_3$) and three levels of the time factor (12, 24 and 48 h). 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 unreactive 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.

4.3 Results

4.3.1 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^{-1} (corresponding to loads of 2.48 and 1.49 mg m^{-2}), respectively (Fig. 4.1, Table 4.2). At all TIs, P losses of all forms increased significantly (p<0.05) with slurry application compared with the soil only treatment (Fig. 4.1). 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 4.2) 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^{-1}

(corresponding to loads of 45.7 and 18.9 mg m^{-2}), respectively, at TI 1 to 3.6 and 1.1 mg L^{-1} (23.5 and 7.5 mg m^{-2}) at TI 3 (Fig. 4.1).

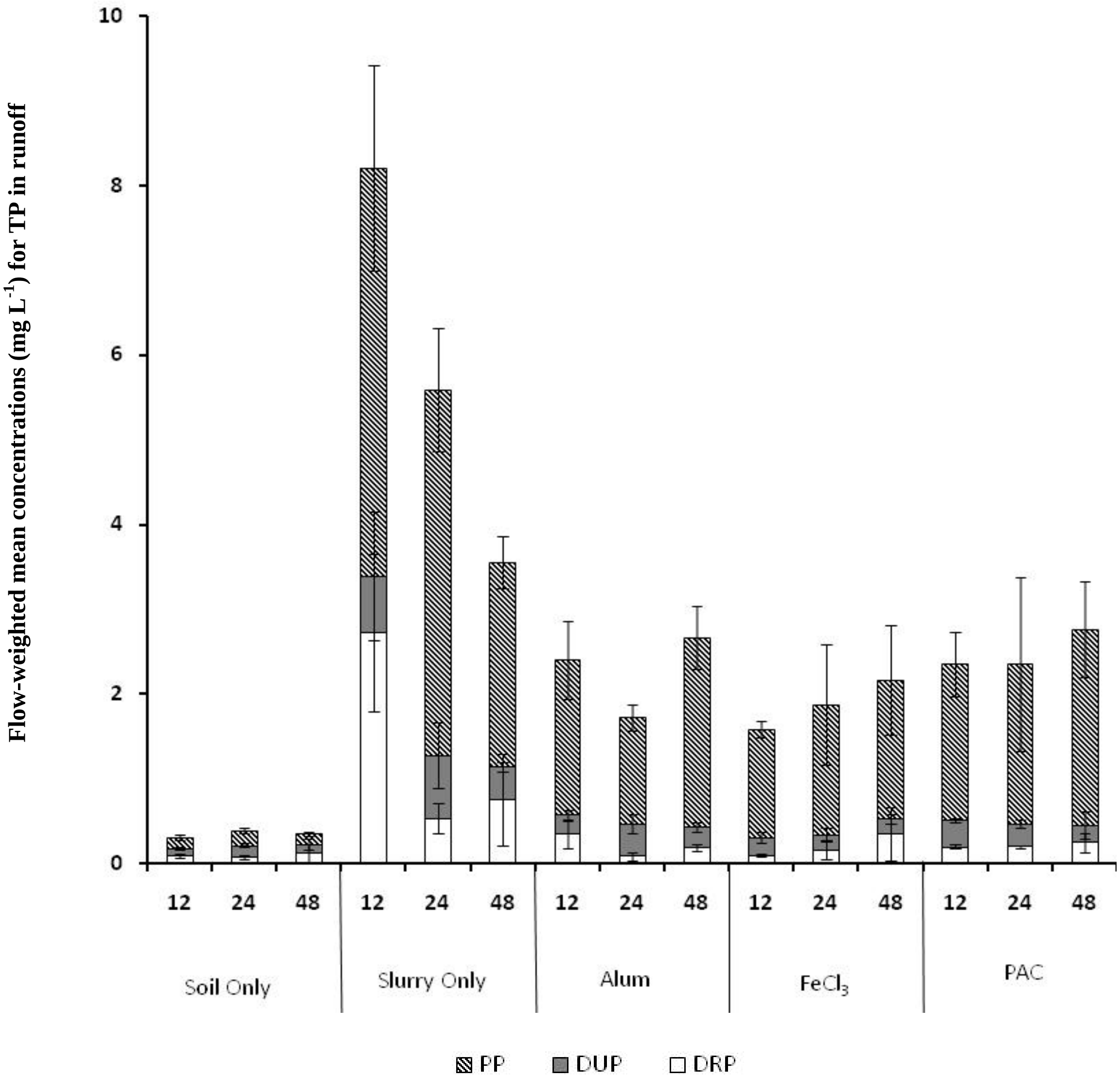

Figure 4.1 Histogram of flow-weighted mean concentrations (mg L^{-1}) for dissolved reactive phosphorus (DRP), dissolved un-reactive phosphorus (DUP) and particulate phosphorus (PP) in runoff at time intervals of 12, 24 and 48 h after land application of pig slurry.

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 48 h (Fig. 4.1). 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 4.2).

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.

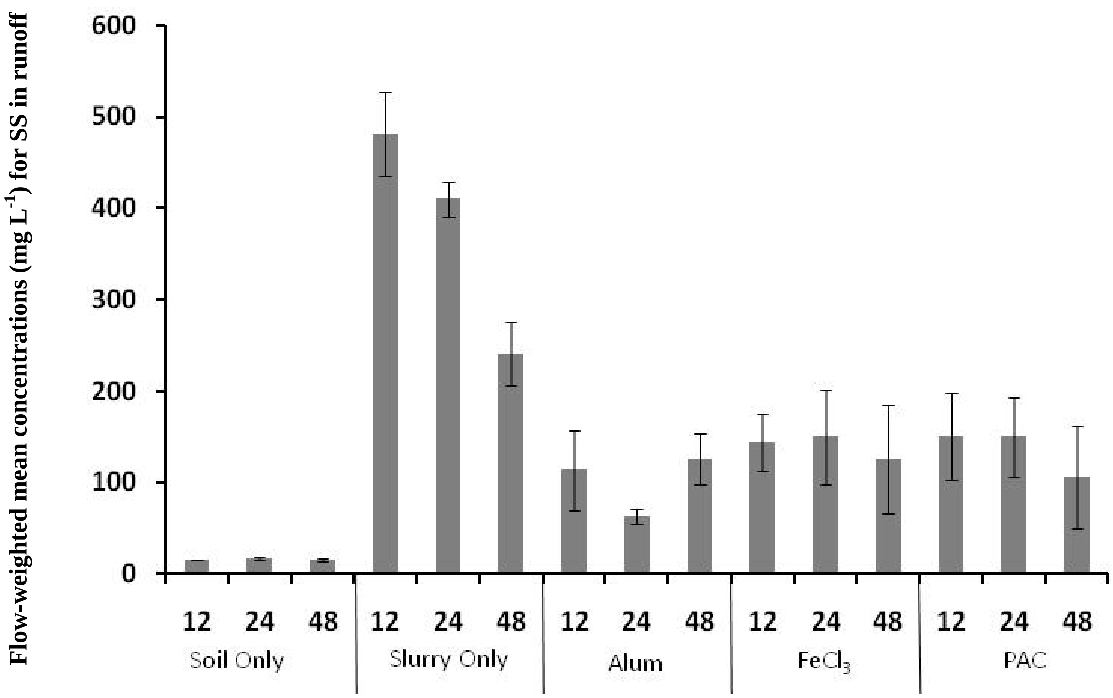

Figure 4.2 Histogram of average flow-weighted mean concentration of suspended solids (SS) (mg L^{-1}) in runoff at time intervals of 12, 24 and 48 h after land application of pig slurry.

4.3.2 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^{-1} (corresponding to loads of 134, 116 and 118 mg m^{-2}) after TIs 1, 2 and 3, respectively (Fig. 4.2). 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^{-1} or 2780 mg m^{-2}). 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.

4.4 Discussion

4.4.1 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^{-1} (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 water body that might be expected at field-scale.

4.4.2 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^{-1} and found that at 30 min rainfall events, each with an intensity of 100 mm h^{-1}, DRP concentrations in runoff reduced from 8.4 mg DRP L^{-1} at a TI of 1 day to 2.6 mg DRP L^{-1} at a TI of 29 days. Allen and Mallarino (2008) spread pig slurry in a plot study at varying rates up to 108 kg P ha^{-1} and found that during 30-min rainfall events, each with an intensity of 76 mm h^{-1}, DRP and TP loads in runoff were 3.8 and 1.6 times lower at a TI of 10-16 days than at a TI of less than 24 h. 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 24 h after application, and confirms that the prohibition of the land-spreading of slurry, if heavy rain is forecast in the next 48 h (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).

4.4.3 The effect of slurry amendment on P losses

The use 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 4.2). 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 $AlCl_3$, 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 $AlCl_3$, 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 $AlCl_3$ at 1:1 Al/TP.

Investigation of chemical amendment effectiveness on two soils using identical amendments, spreading rate and TI (Table 4.3) 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 in Chapter 3, incidental losses from slurry were higher, but not significantly so. Additionally, the effectiveness of the amendments (PAC, in particular) was much lower than reported in Chapter 3 (Table 4.3). This may be explained by differences in soil characteristics between the two experiments: the soil used in Chapter 3 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 4.2). The effectiveness of slurry amendments is, hence, soil specific and should therefore be examined in future studies.

Table 4.3 Comparison of flow-weighted mean concentrations (mg L^{-1}) of TP in runoff from two different soils with identical amendments, spreading rates and TIs[a]

	Soil 1		Soil 2	
Study	Current study		Chapter 3	
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 (mg L^{-1})	2.8±0.5		16.72±3.58	
Runoff results	TP mg L^{-1}	Removal (%)	TP mg L^{-1}	Removal (%)
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%
$FeCl_3$	2.17	41%	1.14	57%

[a]Runoff results are from rainfall events at TIs of 48 h, which occurred in both 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.

4.4.4 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 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_3) emissions from slurry (Lefcourt and Messinger 2001). However, the results from this laboratory experiment, similar to previous studies (Smith et al. 2004; Chapter 3), 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.

4.4.5 Targeted use of amendments

Due to high costs involved (Chapter 2), 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 programme 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 in Chapter 3 (Table 4.3) 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.

4.6 Conclusions

The excessively high losses of P in runoff at TIs of less than 48 h 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 48 h (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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Summary

This chapter investigated the performance of chemical amendments for pig slurry at time intervals of less than 48 h and showed that chemical amendment may be more effective than current time interval-based legislation at reducing incidental P losses. The next chapter attempts to investigate the effect of using chemically amended slurry on leachate, soil properties and greenhouse gas emissions.

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Chapter 5

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

Introduction

This chapter assesses the impacts of chemically amended pig slurry on leachate nutrient losses, soil properties and greenhouse gas (GHG) emissions, and has been published in the Journal of Environmental Management (O' Flynn et al., 2013. Impact of chemically amended pig slurry on greenhouse gas emissions, soil properties and leachate, 128, 690-698). Cornelius O' Flynn developed the experimental design and collected, analyzed and interpreted the leachate, soil and GHG experimental data. He is the primary author of this article. Drs. Mark Healy, Owen Fenton, Gary Lanigan and Shane Troy contributed to the research design and paper writing. Cathal Somers aided in gas sample analysis.

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

Cornelius J. O' Flynn[a], Mark G. Healy [a*], Gary J. Lanigan[b], Shane M. Troy[c], Cathal Somers[b], Owen Fenton[b]

[a]Civil Engineering, National University of Ireland, Galway, Co. Galway, Ireland.
[b]Teagasc, Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland.
[c]Scottish Rural College, Roslin Institute Building, Edinburgh, UK.
*Corresponding author. Tel: +353 91 495364; fax: +353 91 494507. E-mail address: mark.healy@nuigalway.ie

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% 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]. Columns filled with sieved soil were incubated for 8 mo at 10^{o}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 N_2O and CO_2 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

5.1 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 (Pm)). 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. Chapter 2 and Chapter 3 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 (Chapter 2) and then using a laboratory rainfall simulator (Chapter 3). In the latter study (Chapter 3), 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 (CH_4) from enteric fermentation and manure management and nitrous oxide (N_2O) 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 (Chapter 2; Chapter 3), 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, due to changes in slurry chemistry and pH, chemical amendment of pig slurry: (1) reduced leached losses of N, P and carbon (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.

5.2 Materials and Methods

5.2.1 Slurry collection and characterization

Table 5.1 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. [a]Values changed to mg L^{-1} assuming densities of 1 kg L^{-1}.

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. 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^{o}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

Whatman No. 2 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^{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 5.1.

5.2.2 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 Chapters 2 and 3. 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 5.2.

Table 5.2 Characterisation of amendments used in this study (Chapters 2 and 3).

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		
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

5.2.3 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 (Pm, 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 (PO_4^{3-}-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 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):

$$\frac{C_e}{x/m} = \frac{1}{ab} + \frac{C_e}{b} \qquad [5.1]$$

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):

$$S' = k_d C - S_0 \qquad [5.2]$$

where S′ is the mass of P adsorbed from solution (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):

$$WFPS = \frac{WC * \rho_b}{n} \qquad [5.3]$$

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 (NH_4^+-N, NO_3^--N and nitrite-N (NO_2^--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 Whatman No. 2 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.

5.2.4 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 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^o C at 75% humidity, based on typical climatic conditions in Ireland (Walsh, 2012). All columns received 160 ml of distilled water per wk, 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.

5.2.5 Leachate collection and analysis

The leachate from each column was collected and sampled weekly from week 0. Upon collection, samples were weighed and a subsample was passed through a 0.45-μm filter and analysed colorimetrically for DRP, NO_2^-, NH_4^+ and total oxidized nitrogen (TON) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Nitrate was calculated by subtracting NO_2^- from TON. Filtered and unfiltered subsamples were tested for total dissolved phosphorus (TDP) and TP using acid persulfate digestion and analysed colorimetrically using a nutrient analyser (Konelab 20). 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.

5.2.6 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), Pm, 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-μm syringe filter, prior to being analysed 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.

Figure 5.1 PVC column with rubber stopper.

5.2.7 Greenhouse gas emissions

Direct GHG emissions (N_2O, carbon dioxide (CO_2) and CH_4) were analysed 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 tops of the PVC columns were sealed using rubber stoppers (Fig. 5.1). 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, CO_2 and CH_4 concentrations were analysed using a gas chromatograph (Varian CP 3800 GC, Varian, USA) fitted with a 63Ni electron capture detector (ECD) for N_2O analysis, a thermal conductivity detector (TCD) for CO_2 analysis, and a flame ionization detector (FID) for CH_4 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:

$$\frac{dGas}{dt} * 10^{x} * \frac{V_{chamber} * p * 100 * MW}{R * T} * 10^{y} * \frac{1}{A} \qquad [5.4]$$

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 on which compound in which the emissions are expressed; *R* is a gas constant, 8314 J mol^{-1} 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 mg m^{-2} 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.

5.2.8 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.

5.3 Results

5.3.1 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±0.24% (data not shown). Comparatively, at the same time, slurry-only, alum, $FeCl_3$ and PAC treatments had WCs of 31.76±0.44%, 32.45±0.35%, 31.89±0.78%, and 32.13±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.

5.3.2 Nitrogen leachate and soil properties

There were no statistically significant differences between treatments for TN in soil (Table 5.3). 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. 5.2 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 5.3). Nitrite loads peaked between wks 10 and 26 (Fig. 5.2 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 NH_4^+-N kg^{-1} soil, respectively). This compared with values of 44.0 and 48.9 g NH_4^+-N kg^{-1} soil for soil-only and slurry-only, respectively.

Table 5.3 Average soil phosphorus, nitrogen and carbon contents by sampling time and depth.

	Month	Depth (m)	Treatment				
			Soil Only	Slurry	Alum	$FeCl_3$	PAC
Morgan's P ($mg\ L^{-1}$)	1	0-0.05	3.53^{a}	7.79^{c}	4.19^{ab}	4.64^{b}	4.40^{ab}
		0.05-0.1	3.69^{a}	3.80^{a}	3.75^{a}	3.69^{a}	3.68^{a}
		0.1-0.2	3.53^{a}	3.99^{a}	3.79^{a}	3.95^{a}	3.84^{a}
	2	0-0.05	3.84^{a}	6.12^{b}	4.41^{a}	4.61^{a}	4.52^{a}
		0.05-0.1	4.02^{a}	4.03^{a}	3.85^{a}	3.80^{a}	3.99^{a}
		0.1-0.2	4.14^{a}	4.31^{a}	3.88^{a}	3.86^{a}	4.08^{a}
	3	0-0.05	3.19^{a}	6.28^{c}	4.22^{b}	4.55^{b}	4.28^{b}
		0.05-0.1	3.14^{a}	3.17^{a}	3.50^{a}	3.60^{a}	3.39^{a}
		0.1-0.2	3.35^{a}	3.55^{a}	3.71^{a}	3.78^{a}	3.67^{a}
	6	0-0.05	2.69^{a}	4.60^{c}	3.44^{ab}	4.18^{bc}	3.52^{ab}
		0.05-0.1	3.22^{a}	3.41^{a}	3.21^{a}	3.62^{a}	3.10^{a}
		0.1-0.2	3.51^{a}	3.67^{a}	3.65^{a}	3.61^{a}	3.28^{a}
	8	0-0.05	2.17^{a}	3.42^{c}	2.63^{ab}	3.00^{bc}	3.38^{c}
		0.05-0.1	2.44^{a}	2.39^{ab}	2.67^{ab}	2.95^{ab}	3.16^{b}
		0.1-0.2	2.66^{a}	3.14^{a}	3.01^{a}	3.38^{a}	3.66^{a}
WEP ($mg\ kg^{-1}$)	1	0-0.05	0.54^{a}	1.13^{b}	0.49^{a}	0.57^{a}	0.59^{a}
		0.05-0.1	0.56^{a}	0.58^{a}	0.54^{a}	0.58^{a}	0.57^{a}
		0.1-0.2	0.64^{a}	0.56^{a}	0.57^{a}	0.60^{a}	0.54^{a}
	2	0-0.05	0.51^{a}	0.99^{b}	0.57^{a}	0.57^{a}	0.55^{a}
		0.05-0.1	0.49^{a}	0.47^{a}	0.49^{a}	0.45^{a}	0.50^{a}
		0.1-0.2	0.50^{a}	0.46^{ab}	0.39^{b}	0.43^{ab}	0.45^{ab}
	3	0-0.05	0.62^{a}	1.06^{b}	0.69^{a}	0.71^{a}	0.73^{a}
		0.05-0.1	0.65^{a}	0.66^{a}	0.61^{a}	0.67^{a}	0.62^{a}
		0.1-0.2	0.64^{a}	0.70^{a}	0.65^{a}	0.63^{a}	0.62^{a}
	6	0-0.05	0.54^{a}	0.87^{b}	0.60^{a}	0.63^{a}	0.52^{a}
		0.05-0.1	0.54^{a}	0.55^{a}	0.50^{a}	0.52^{a}	0.49^{a}
		0.1-0.2	0.49^{a}	0.51^{a}	0.47^{a}	0.47^{a}	0.44^{a}
	8	0-0.05	0.58^{a}	0.79^{b}	0.55^{a}	0.56^{a}	0.62^{ab}
		0.05-0.1	0.58^{a}	0.62^{a}	0.55^{a}	0.53^{a}	0.57^{a}
		0.1-0.2	0.55^{a}	0.61^{a}	0.58^{a}	0.57^{a}	0.56^{a}
TC (%)	1	0.05-0.1	1.70^{a}	1.73^{a}	1.86^{a}	1.69^{a}	1.74^{a}
	2	0.05-0.1	1.78^{a}	1.73^{a}	1.77^{a}	1.76^{a}	1.68^{a}
	3	0.05-0.1	1.72^{a}	1.73^{a}	1.74^{a}	1.84^{a}	1.68^{a}
	6	0.05-0.1	1.81^{a}	1.78^{a}	1.74^{a}	1.79^{a}	1.66^{a}
	8	0.05-0.1	1.75^{a}	1.73^{a}	1.73^{a}	1.79^{a}	1.75^{a}
TN (%)	1	0.05-0.1	0.18^{a}	0.18^{a}	0.20^{a}	0.19^{a}	0.19^{a}
	2	0.05-0.1	0.18^{a}	0.18^{a}	0.18^{a}	0.19^{a}	0.18^{a}
	3	0.05-0.1	0.18^{a}	0.18^{a}	0.18^{a}	0.19^{a}	0.18^{a}
	6	0.05-0.1	0.19^{a}	0.19^{a}	0.18^{a}	0.18^{a}	0.18^{a}
	8	0.05-0.1	0.19^{a}	0.19^{a}	0.18^{a}	0.18^{a}	0.18^{a}
C:N Ratio	1	0.05-0.1	9.53^{a}	9.39^{a}	9.32^{a}	9.07^{a}	9.30^{a}
	2	0.05-0.1	9.73^{a}	9.89^{a}	9.69^{a}	9.41^{a}	9.30^{a}
	3	0.05-0.1	9.54^{a}	9.61^{a}	9.51^{a}	9.80^{a}	9.39^{a}
	6	0.05-0.1	9.38^{a}	9.43^{a}	9.78^{a}	9.78^{a}	9.32^{a}
	8	0.05-0.1	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 ($p < 0.05$)

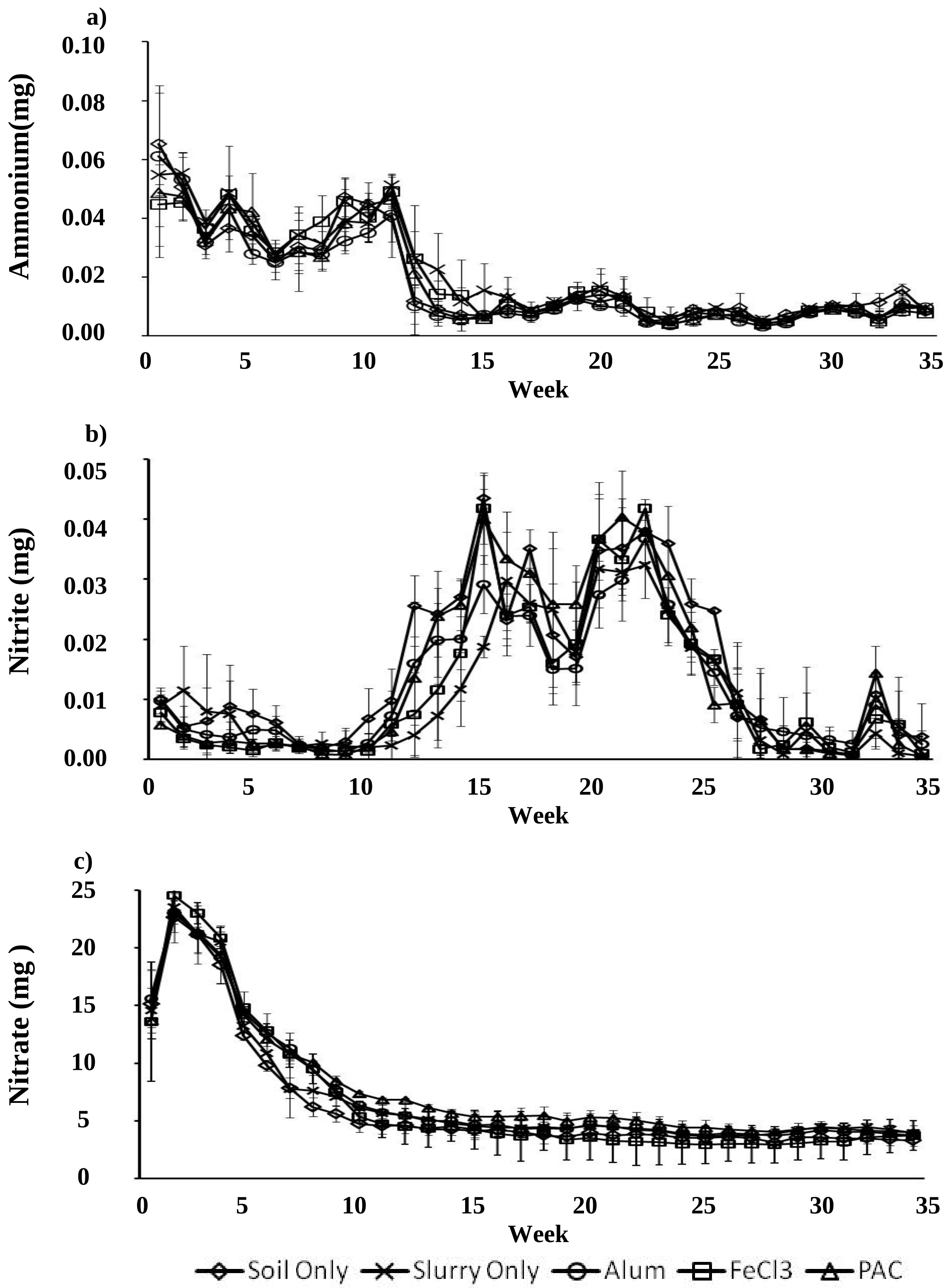

Figure 5.2 Average weekly loads (± standard deviation) of ammonium a) nitrite b) and nitrate c) leached column^{-1}.

5.3.3 Nitrous oxide emissions

Nitrous oxide emissions from the soil-only treatment remained fairly constant throughout the 28-d study (Fig. 5.3 a), with cumulative emissions of 22±8 mg N_2O-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 N_2O-N m^{-2}. The highest cumulative losses of 188±86 mg N_2O-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.

5.3.4 Phosphorus leachate and soil properties

There were no significant differences in the quantity of P leached between treatments (data not shown), 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 5.3). 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 5.3). 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 5.3).

5.3.5 Carbon leachate

The average cumulative amount of TOC and TIC leached is shown in Fig. 5.4 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. 5.4 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.

5.3.6 Carbon emissions

Emissions of CO_2 followed a similar trend to N_2O emissions (Fig. 5.3 b). The soil-only treatment had the lowest emissions, with cumulative losses of 36±4 g CO_2-C m^{-2}. Losses increased upon application of slurry, but were only statistically significantly different (p=0.008) in the case of $FeCl_3$-amended slurry, which had cumulative losses of 106±23 g CO_2-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. 5.3 c), but no treatment had significantly higher losses than the soil-only treatment. After 5 d, all treatments either gained or lost CH_4, with $FeCl_3$–amended slurry acting overall as a net sink with cumulative losses of -13±7 mg CH_4-C m^{-2}, whilst PAC-amended slurry had cumulative losses of 13±6 mg CH_4-C m^{-2}.

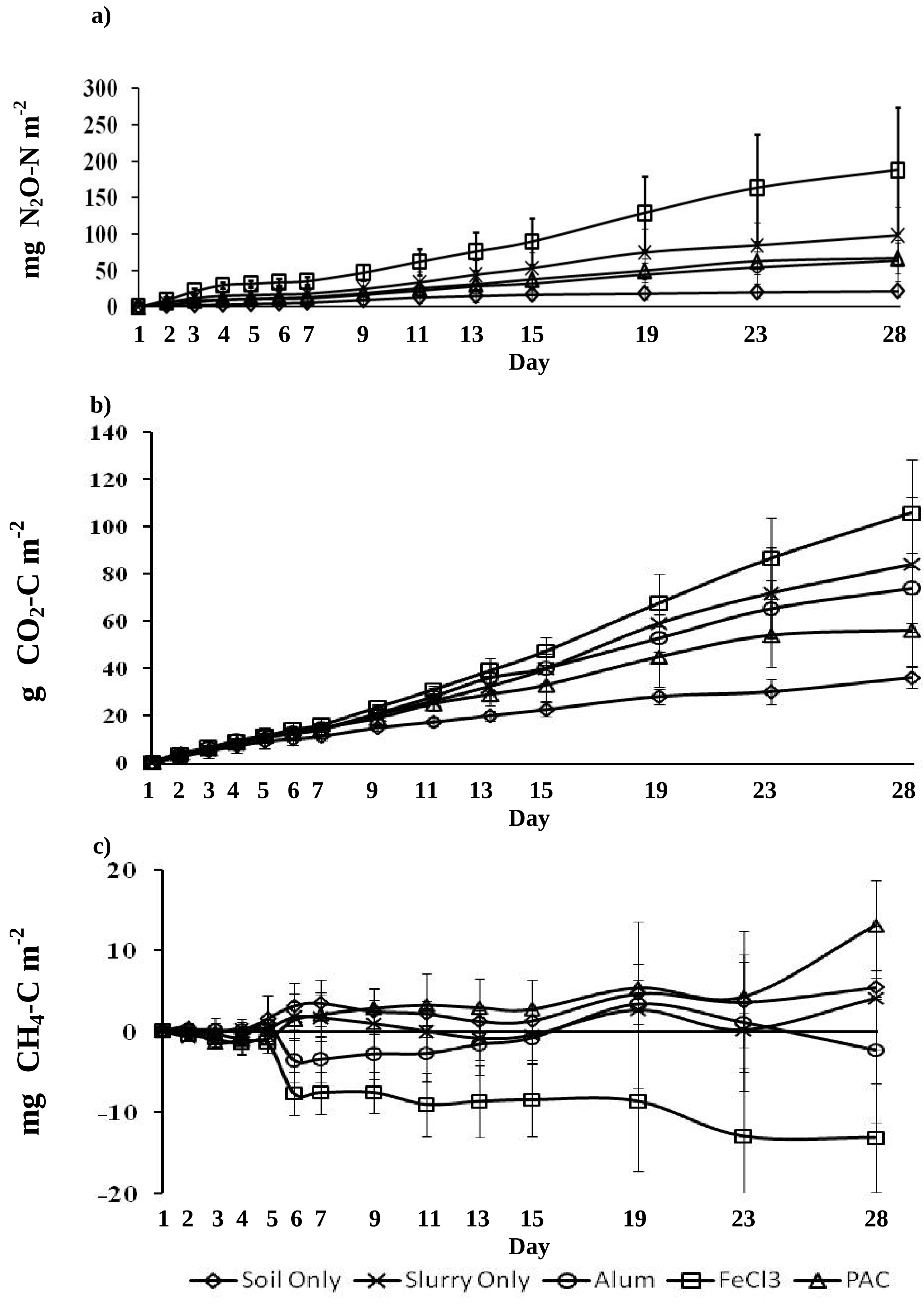

Figure 5.3 Cumulative gaseous emissions (± standard deviation) of N_2O-N (a) CO_2-C (b) and CH_4-C (c) from columns at each sampling period.

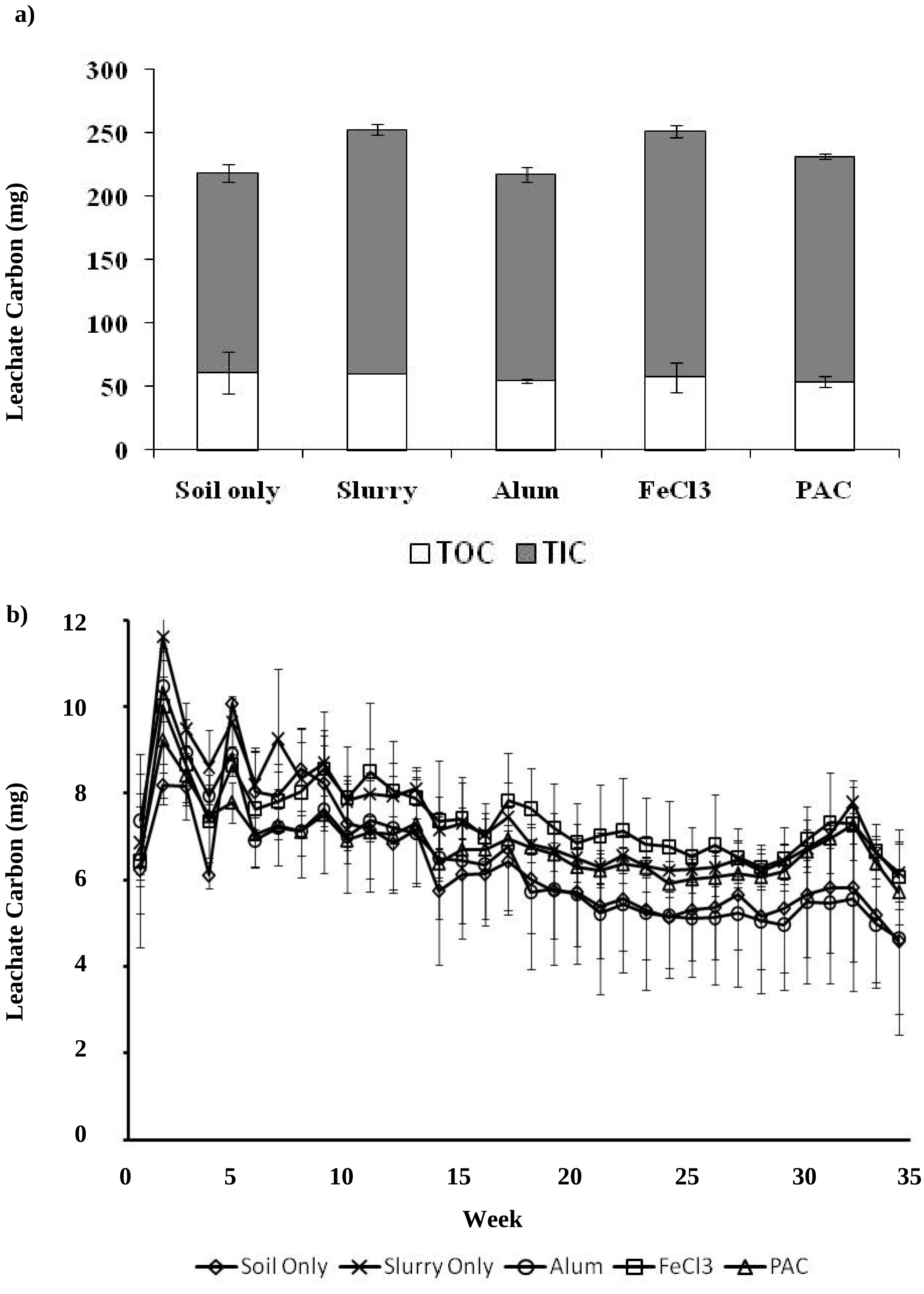

Figure 5.4 Cumulative loads of total organic carbon (TOC) and total inorganic carbon (TIC) leached over the duration of the experiment a) and weekly loads of total carbon leached from columns b) (± standard deviation).

5.4 Discussion

5.4.1 Nitrogen leachate and soil properties

Denitrification is the mainly microbial reduction of NO_3^- to the gaseous products nitric oxide (NO), N_2O, or inert di-nitrogen (N_2). 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 mineralisation, leaching, plant uptake and denitrification (Porporato et al., 2003).

The early peak in NO_3^- 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 NH_4^+ (Fig. 5.2 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 N_2 and N_2O 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 5.3). 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 due to the preference of denitrifiers for NO_3^-, even when both are present (Rivett et al., 2008).

High NH_3^+ volatilisation 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 volatilisation 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 volatilisation 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 5.3) due to the large background amounts of soil inorganic N, which was a result of the occurrence of mineralisation. 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 volatilisation losses.

5.4.2 Nitrous oxide emissions

The increased cumulative release of N_2O after slurry application was as expected (Velthof et al., 2003). The cumulative N_2O 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 been previously 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 NO_3^- and organic carbon content (Section 5.4.4) (Velthof et al., 2003). The drying and rewetting of the soil during construction provided conditions which facilitated C and N mineralisation and denitrification, and would also have facilitated N_2O release to the atmosphere (Porporato et al., 2003).

The increase in N_2O emissions associated with $FeCl_3$ addition may be explained as a result of ammonia volatilisation abatement. The difference in soil NH_4^+ levels between treatments 7 d after application may be 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 $FeCl_3$ addition, principally due to a reduction in slurry pH (Molloy and Tunney, 1983).

5.4.3 Phosphorus leachate and soil properties

Unlike previous runoff studies (Chapter 3), 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 Chapter 3, which 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±0.29 mg L^{-1}) was used in this experiment, its high adsorption capacity for P (0.224 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 in Chapter 2, which 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. It is assumed that this P was adsorbed by the soil's high adsorption capacity for P, but was not detected by WEP or Pm analysis. This shows the limitations of using particular tests in measuring soil P.

5.4.4 Carbon leachate and emissions

The decrease in loads of TC leached after wk 2 may have been due to the increased mineralisation of C and N, which may have been the cause of increased losses of CO_2 to the atmosphere. This loss of CO_2 to the atmosphere may also be the reason that there were statistically no significant differences between treatments for TC in soil (Table 5.3). 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 CO_2 emissions (Bol et al., 2004; Dumale et al., 2009; Cayuela et al., 2010). The increased CO_2 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 5.3).

After land application, CH_4 emissions are generally of minor importance compared to N_2O emissions (Wulf et al., 2002a, 2002b), as CH_4 emissions from enteric fermentation and during slurry storage are much more important (Chadwick et al., 2000). This is due to CH_4 being produced by decomposition of OM in faecal matter under anaerobic conditions. After landspreading, OM is oxidised to CO_2 and H_2O in the aerobic conditions present. Mineral grassland soils are known to generally be a CH_4 sink, due to either oxidation of CH_4 to CO_2 in soils or incorporation into microbial biomass, with uptake rates ranging from 0.5 – 3.3 mg CH_4 m^{-2} d^{-1} (Mosier et al., 1991; Dobbie et al., 1996; Saggar et al., 2008). The change in trend after d 5 may be due to microbial build-up of methanogens, CH_4 emitting microorganisms, in the anaerobic conditions present. The results from the present study show that no additional risk to CH_4 emissions is posed by the chemical amendment of pig slurry.

5.5 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.

5.6 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 N_2O and CO_2 losses. Moreover, increased N_2O emissions associated with $FeCl_3$ addition were likely to be due to a reduction in ammonia volatilisation, a theory supported by an increase in soil NH_4^+ concentrations.

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Summary

This chapter showed that chemical amendment of pig slurry is possible without any significant impacts on leachate nutrients, reactive N emissions, soil C cycling, or GHG emissions. The following chapter will investigate if soil type is a factor in the performance of amendments.

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Chapter 6

Changes in soil chemistry following application of chemically amended pig slurry

Introduction

This chapter assesses soil type suitability to receive chemically amended pig slurry, by investigating the impact it has on soil chemistry, and has been submitted to Soil Biology and Biochemistry. Cornelius O' Flynn developed the experimental design, and collected, analyzed and interpreted slurry and soil experimental data. He is the primary author of this article. Drs. Mark Healy, Owen Fenton and David Wall contributed to the research design and paper writing.

Changes in soil chemistry following application of chemically amended pig slurry

Cornelius J. O' Flynn[a], Mark G. Healy [a*], David Wall[b], Owen Fenton[b]

[a]Civil Engineering, National University of Ireland, Galway, Co. Galway, Ireland.

[b]Teagasc, Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland.

*Corresponding author. Tel: +353 91 495364; fax: +353 91 494507. E-mail address: mark.healy@nuigalway.ie

Abstract

Cost effective strategies for using chemically amended organic fertilizers need to be developed for successful adoption as a mitigation measure for minimizing nutrient losses to water bodies. Targeting their use within critical source areas or along the nutrient transfer continuum has the potential to reduce costs. However, an appropriate amendment must be selected based on compatibility with a soil's physical and chemical characteristics. From a production perspective, it is important that there should be no reduction in the soil test phosphorus (P) below agronomic optima, whilst from an environmental perspective, losses should be minimized. The current study attempted to investigate the effectiveness of various chemical amendments for achieving these seemingly opposing goals. A 3-mo incubation study was conducted on 18 different soil types, stored at 10^{o}C and 75% humidity, and treated with unamended and amended slurry which was spread at a rate equivalent to 19 kg total P (TP) ha^{-1}. The amendments examined were: commercial grade liquid alum (8% Al_2O_3), applied at a rate of 0.88:1 [Al:TP], and commercial-grade liquid poly-aluminium chloride (PAC) (10% Al_2O_3), applied at a rate of 0.72:1 [Al:TP]. Addition of unamended slurry increased soil water extractable P (WEP) across all soil types, with alum and PAC achieving reductions of soil WEP ranging from 16% to 48% and 0.2% to 40%, respectively. The efficacy of the amendments depended on the soil test P and degree of P saturation, which indicated the importance of identifying appropriate amendments for the diverse range of soil types that may be present on a farm. Poly-aluminium chloride appears to be the most suitable amendment with which to chemically amend pig slurry as, although alum achieved greater

reductions in soil WEP, its use was also associated with greater reductions in plant available P. Due to their high cost, the incorporation of amendments into existing management practices can only be justified where local soil types are suitable.

Keywords: pig slurry; P sorbing amendments; Water Framework Directive; degree of P saturation; soil test phosphorus.

6.1 Introduction

The land application of organic fertilizers, when followed by an episodic rainfall event, can lead to incidental and chronic phosphorus (P) losses in overland flow (Buda et al., 2009), which may lead to eutrophication of receiving waters (Carpenter et al., 1998). Incidental losses take place when a rainfall event takes place shortly after slurry application and before slurry infiltrates the soil, whilst chronic losses are a long-term loss of P from soil as a result of a build-up in soil test P (STP), caused by application of inorganic fertilisers and manure (Buda et al., 2009; Schulte et al., 2010). Pig farms typically have high levels of STP due to their high stocking rates and P surplus, which results in an increased potential of chronic P losses - particularly in Critical Source Areas (CSAs; Doody et al., 2012), where sources of P coincide with hydrologically active zones which are connected to waterbodies. As pig slurry is commonly landspread (Nolan et al., 2012), various mitigation methods, mainly governed by legislation (exclusion zones, timing and magnitude of application), are used. Previous research (Smith et al., 2001, 2004; Dou et al, 2003; Chapters 2, 3 and 4) has demonstrated that chemical amendment of pig slurry is an effective means of reducing incidental P losses in runoff. However, to date no study has considered the role of soil type on the efficacy of chemical amendments, nor has any study attempted to quantify the efficacy of chemical amendments to pig slurry (or any other wastewater type) within a holistic framework, which considered not only soil type but also surface runoff, subsurface leachate, and greenhouse gas (GHG) emissions.

The efficacy of chemical amendment of pig slurry on incidental surface and subsurface losses of P have been considered by the authors (Chapters 2, 3, 4 and 5) and others (Smith et al., 2001, 2004). In Chapter 3, it was found that poly-aluminium chloride (PAC), followed by ferric chloride ($FeCl_3$) and alum (8% Al_2O_3), was most effective in reducing surface losses of total phosphorus (TP) from laboratory runoff boxes when subject to rainfall events with an intensity of 10.3±0.15 mm h^{-1} at times ranging from 48 to 96 h following slurry application. However, the efficacies of the chemical amendments in reducing surface losses appeared to be related to soil type (Chapters 3 and 4). Impacts on subsurface losses and GHG emissions were also examined in Chapter 5, where pig slurry and chemically amended pig slurry were applied at approximately the same rate as surface runoff studies (19 kg TP ha^{-1}, 90 kg total nitrogen (TN) ha^{-1} and 180 kg total carbon (TC) ha^{-1}) to soil columns and, over an 8-mo study period, found that chemical amendment did not significantly change GHG emissions (compared to pig slurry-only applications), nor was there any significant change in P leached from the soil examined.

Due to their high cost, chemical amendments to pig slurry should only be used in targeted areas, where they are most effective. This will involve identification of CSAs – but will also involve consideration of incidental and chronic losses arising from the various soil types in these areas.

Before work can be advanced on the use of chemically amended pig slurry to agricultural grasslands, it is critical that soil type is considered when examining the potential of amendments to reduce chronic P losses. To date, such studies have mainly considered one soil type. For example, Kalbasi and Karthikeyan (2004) examined the effect of chemically amending dairy cattle slurry with alum, $FeCl_3$, and lime on silt loam soils with three different STP levels (12, 66, and 94 mg kg^{-1} Bray-1 P, respectively) in an incubation experiment conducted over 24 mo. Kalbasi and Karthikeyan (2004) found that the effect of chemical amendment depended on treatment type, P application rate and background STP level, and also recommended that more work was needed to investigate the effectiveness of amendments in soils varying in physical and chemical characteristics. Moore and Edwards (2007) found that following long-term (7 yr) land application of alum-amended poultry litter on a silt loam soil, runoff P and soil water extractable phosphorus (WEP) was reduced in plots receiving alum-treated poultry manure. Brennan et al. (unpublished data) added chemically amended dairy cattle slurry to five different soil types, at a rate equivalent to 33 m^3 ha^{-1} in a laboratory incubation study with a total duration of 9 mo and found differing effects on WEP between soil types. Chemically amended slurry reduced the WEP of the soils (compared to unamended slurry) by between 52 and 73% for alum, 0 and 38% for $FeCl_3$, and

21 and 64% for PAC. These differences may be due to the differing chemical makeup of soils, with varying amounts of aluminium, silicate particles and surface area available to retain P. In an incubation study, Shreve et al. (1996) added unamended poultry litter, and poultry litter amended with either alum (100 or 200 g kg^{-1}), lime (25 or 50 g kg^{-1}) or $FeSO_4$ (100 or 200 g kg^{-1}) to soils with pHs between 4.0 and 8.0. They found that both unamended and amended slurry significantly increased soil soluble reactive P (SRP) compared to soil-only, that amendments significantly reduced SRP levels, and that an apparent equilibrium in SRP levels was attained 98 d after treatment. Previous research (Tunney, 2000; Regan et al., 2010) has shown a significant relationship between STP (based on WEP, Morgan's P (P_m) and Mehlich P (M3P)) and runoff dissolved reactive P (DRP). Therefore, it is essential that soil type is considered when proposing potential methods to mitigate losses of P in runoff.

The hypothesis of this study was that soil type is significant in determining the efficacy of chemically amended pig slurry in reducing surface and subsurface losses of P. To address this, 18 soils, of various textural classes and initial STP concentrations, received pig slurry and chemically amended pig slurry, and were stored in a temperature and humidity-controlled environment for 3 mo. At the end of this period, the impact of the amendments on the soil WEP, P_m and M3P were quantified with the aim of determining the most suitable soil type on which to spread chemically amended pig slurry. Using these data and the previous research conducted by the authors on incidental losses of nutrients (surface and subsurface losses and GHG emissions), the study aimed to identify the best amendment.

6.2 Materials and Methods

6.2.1 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 November 2012. The sampling point was a valve on an outflow pipe between two holding tanks. 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 at 10^{o}C in a 25-L drum prior to testing. The TP was 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 6.1.

Table 6.1 Physical and chemical characteristics of the pig slurry used in this experiment and characteristic values of pig slurry from other farms in Ireland.

TP	NH_4^+-N	pH	DM	Reference
(mg L^{-1})			(%)	
525±27	2171±30	7.29±0.14	5.14±0.26	The present study
800				S.I. No. 610 of 2010
1630			5.77	McCutcheon, 1997[a]
900±7			3.2±2.3	O' Bric, 1991[a]

TP, total P; TN, total N; TK, total K; DM, dry matter. [a]Values changed to mg L^{-1} assuming densities of 1 kg L^{-1}.

Table 6.2 Characterisation of amendments used in this study.

Amendment		Alum	PAC
		8% Al_2O_3	10 % Al_2O_3
pH		1.25	1.0 – 3.0
WEP	mg kg^{-1}	0	
Al	%	4.23	
Fe	%	<0.01	
As	mg kg^{-1}	1	<1.0
Cd	mg kg^{-1}	0.21	<0.2
Cr	mg kg^{-1}	2.1	<2.0
Ni	mg kg^{-1}	1.4	<1.0
Pb	mg kg^{-1}	2.8	<2.0
Sb	mg kg^{-1}		<1.0
Se	mg kg^{-1}		<1.0
Hg	mg kg^{-1}		<0.2

6.2.2 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 in Chapters 2 and 3. 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] and (2) commercial-grade liquid PAC (10 % Al_2O_3) applied at a rate of 0.72:1 [Al:TP]. Ferric chloride, examined by the authors in previous studies (Chapters 3 and 4), was not included in the present study, as it was found in Chapter 5 that its use was associated with elevated GHG emissions. The compositions of the amendments used are shown in Table 6.2.

6.2.3 Soil collection and analysis

Samples of the plough layer (top 0.2 m), selected to represent a variety of STP and textural classes, were collected from 18 sites across Ireland (Fig. 6.1; Table 6.3). The soils were 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 P_m (the national test used for the determination of plant available P in Ireland) using Morgan's extracting solution (Morgan, 1941), and M3P using M3 extracting solution (Mehlich, 1984). Mehlich-3 Al and iron (Fe) (M3-Al and M3-Fe) were used to estimate degree of P saturation in the soils using the equation (Maguire and Sims, 2002):

$$DPS(\%) = \frac{M3P \times 100}{(M3 - Al + M3 - Fe)} \qquad [6.1]$$

where M3P, M3-Al and M3-Fe are the molar concentration of the Mehlich 3 extractable P, Al and Fe (mmol kg^{-1}), respectively. Mehlich-3 calcium (Ca), cobalt (Co), copper (Cu), potassium (K), magnesium (Mg), manganese (Mn) and zinc (Zn) were also analysed using M3 extracting solution (Mehlich, 1984). Soil WEP (100:1 deionised water: soil) was determined after McDowell and Sharpley (2001). Soil pH (n=3) was determined using a pH probe (WTW, Germany) and a 2:1 ratio of deionised water-to-soil. The particle size distribution was determined using a sieving and pipette method (B.S.1377-2; BSI, 1990).

Table 6.3 Soil physical and chemical properties.

Soil	Texture	Soil pH	WEP	P_m	DPS	M3P	M3-Al	M3-Ca	M3-Co	M3-Cu	M3-Fe	M3-K	M3-Mg	M3-Mn	M3-Zn
			mg kg^{-1}	mg L^{-1}	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
A	Medium Loam	5.37	2.15	8.27	7.97	69	749	1867	0.323	3.01	122	229	169	146	6.67
B	Medium Loam	4.91	4.2	4.13	12.81	139	947	1332	0.597	2.13	135	56	123	190	11.09
C	Medium Loam	5.77	4.85	9.53	12.2	127	910	1304	0.511	2.23	129	77	122	163	9.8
D	Sandy loam	5.13	6.7	1.38	12.43	137	966	1383	0.514	2.48	138	64	282	162	10.63
E	Loamy sand	4.74	7.75	6.89	6.42	50	676	2181	0.375	3.58	106	110	121	138	10.2
F	Medium Loam	4.85	8.95	5.97	6.53	52	688	2181	0.414	3.64	108	428	174	141	10.62
G	Sandy loam	4.65	9.05	6.31	6.9	53	542	1224	0.083	2.95	229	72	135	140	6.28
H	Clay loam	5.15	9.95	2.24	3.13	38	1003	1310	0.203	7.12	226	214	126	202	2.6
I	Silt loam	6.57	11.75	7.46	12.22	124	744	955	0.042	0.18	270	325	167	50	3.91
J	Silty clay loam	5.53	12.65	2.64	12.42	129	907	1347	0.506	2.75	127	77	87	159	10.87
K	Medium Loam	5.71	13.65	10.1	8.07	75	808	1905	0.345	3.21	116	367	176	154	7.02
L	Medium Loam	5.72	16	12.13	11.19	78	515	1343	0.421	4.49	182	247	149	122	4.41
M	Sandy loam	5.07	17.2	13.89	10.85	91	519	2459	0.112	3.62	321	112	128	83	8.94
N	Medium Loam	5.44	20.9	14.81	12.38	125	746	970	0.035	0.16	261	143	164	49	3.93
O	Medium Loam	4.97	23	28.47	16.79	204	1042	2467	0.342	13.34	171	323	239	205	10.58
P	Medium Loam	4.84	27.5	23.48	21.51	196	702	1349	0.128	5.58	212	330	334	64	6.64
Q	Medium Loam	4.96	30.4	22.54	16.79	119	540	1520	0.123	3.69	167	219	383	59	6.39
R	Sandy loam	5.03	37.3	30.76	35.68	240	343	1884	0.004	12.68	329	354	269	25	25.99

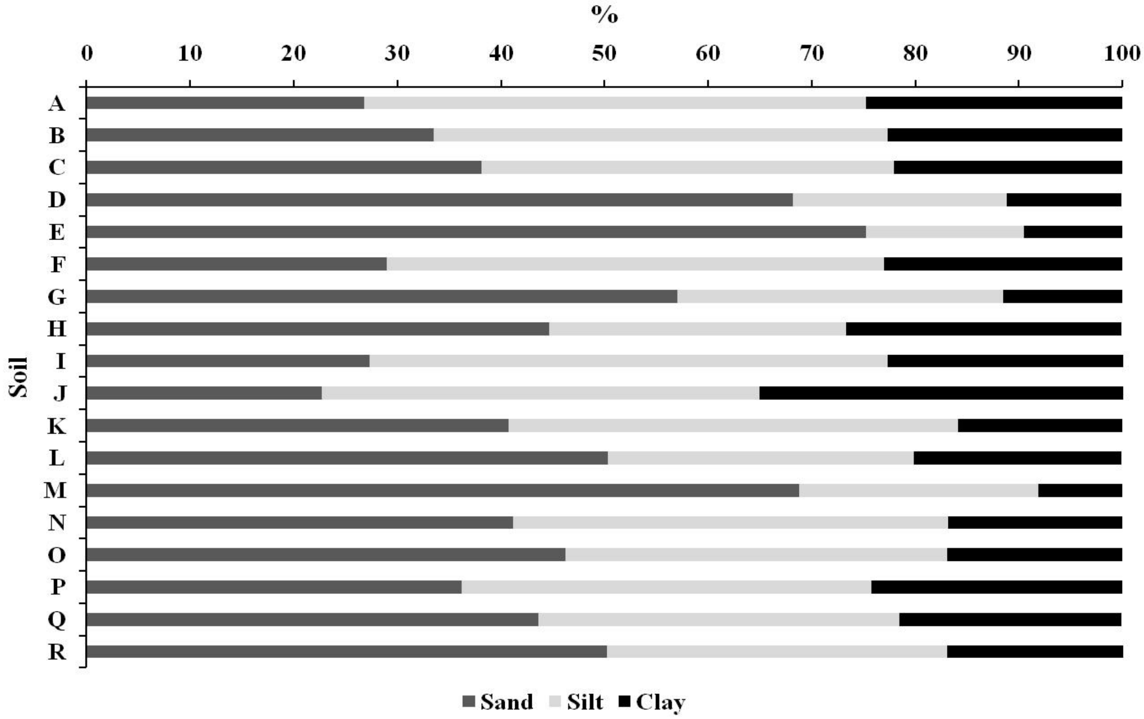


Figure 6.1 Soil particle size distributions.

6.2.4 Incubation experiment

The following treatments were examined in quadruplicate (n=4): (1) soil-only with no slurry applied (2) soil with unamended slurry applied (the study control) and (3) soil receiving amended slurry. Sieved (< 2 mm), oven-dried soil samples (100 g) were placed in 0.5-L containers (70 × 70 mm base). Slurry or amended slurry was added at a rate equivalent to 19 kg TP ha^{-1} and mixed thoroughly before enough deionised water required to achieve 80% water-filled pore space (WFPS) was added. Water-filled pore space, which can impact on rates of denitrification in soil, was estimated in accordance with Haney and Haney (2010):

$$WFPS = \frac{WC * \rho_b}{n} \quad [6.2]$$

where ρ_b is bulk density and n is total porosity (mineral density was taken as 2.65 g cm^{-3}). Less deionised water was added to soils receiving unamended and amended slurry, to take account of the water present in slurry. The soil was then compacted to achieve a bulk density (ρ_b) of 1.2 g cm^{-3}. The containers were covered with para-film, perforated to allow air to circulate, and were stored in a controlled environment for 3 mo at 10°C and 75% humidity. During the study, containers were weighed intermittently and water was added to ensure that approximately 80% WFPS was maintained.

After 3 mo, soils were destructed, oven dried at 40°C for 72 h and crushed to pass a 2-mm sieve before being analysed for WEP, P_m, pH, M3P and M3-Al, Ca, Fe, Co, Cu, K, Mg, Mn and Zn.

6.2.5 Statistical Analysis

The data were analysed in SPSS 20 (IBM, 2011) using a general linear model. Mean values of: WEP, P_m, M3P, pH, DPS, M3-Al, Fe, Ca, Co, Cu, K, Mg, Mn and Zn were analysed when soil-only, the study control, and slurry treated with alum and PAC were applied. Probability values of p>0.05 were deemed not to be significant.

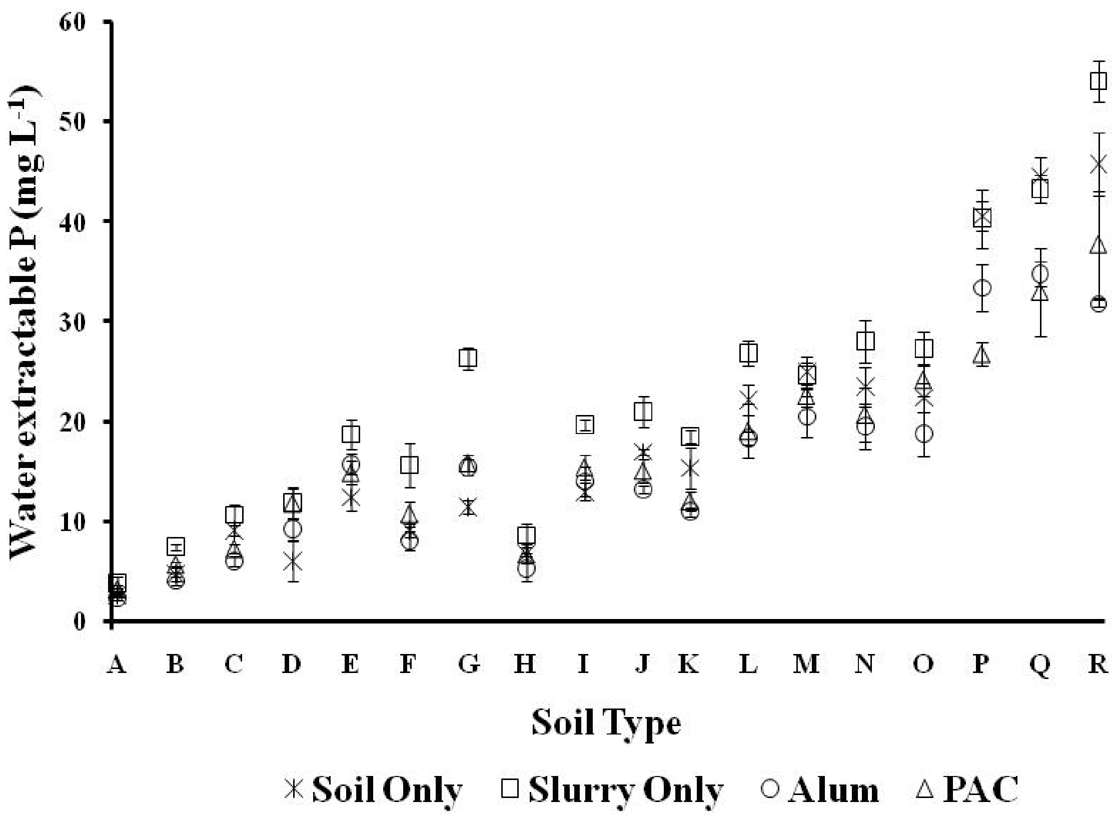


Figure 6.2 Soil water extractable P (mg L^{-1}; ± standard deviation) for each soil type and treatment after incubation.

6.3 Results and Discussion

6.3.1 Water extractable phosphorus

There was a significant interaction between soil type and treatment, but not soil texture, for WEP (p<0.001). Water extractable P values for soil-only ranged from 2.60±0.14 mg kg^{-1} for Soil A to 45.73±3.10 mg kg^{-1} for Soil R (Fig. 6.2). In general, the addition of unamended slurry to soil resulted in increased, but not always significant, levels of WEP, with levels in Soil A increasing to 3.83±0.59 mg kg^{-1} WEP and Soil R increasing to 54.03±2.08 mg kg^{-1} WEP.

In all cases, the addition of amended slurry led to decreased levels of WEP compared to unamended slurry (Fig. 6.2), although not always by a significant amount. The addition of alum resulted in reductions of soil WEP ranging from 16% for Soil E to 48% for Soil F. Addition of PAC produced average reductions ranging from 0.2% for Soil D to 40% for Soil G. Within individual soil types, there were, in general, no statistically significant differences between the levels of WEP in soil treated with either alum or PAC-amended slurry. Averaged across all soil types, the levels of WEP (in decreasing order of WEP) were: unamended slurry > soil only > PAC > alum. Both amendments resulted in significantly decreased (p<0.05) soil WEPs compared to unamended slurry, and the WEPs were not significantly different to soil-only. Amendments performed differently across different soil types and were most effective at reducing WEP in soils with a high DPS. In these soils, there is a need to increase the capacity of the soil to store P. In soils with a low DPS, there is already an abundance of sites to attenuate P and, apart from a potential reduction in incidental losses of nutrients and solids in runoff (Chapter 3), there would appear to be limited long-term benefits. Soil R had a DPS in excess of 100% for all treatments. This means that it was P saturated, and that there were not enough sites to attenuate all of the P present. In the field, such excess P would likely be exported along the transfer continuum.

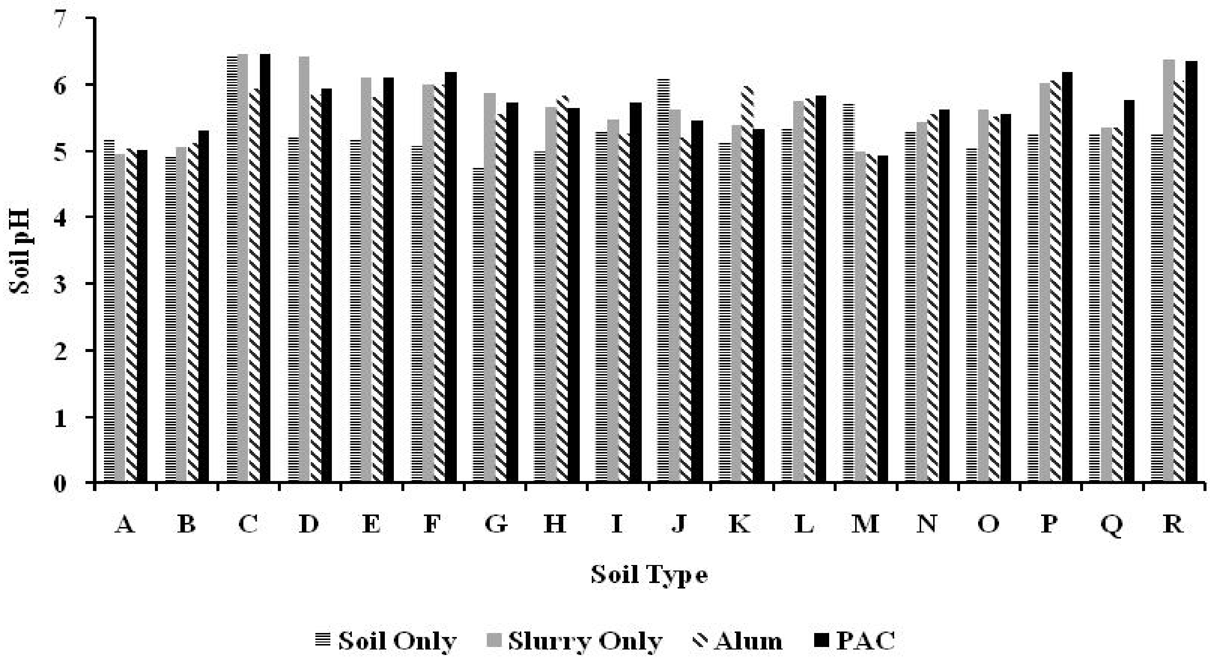


Figure 6.3 Soil pH for each soil treatment.

6.3.2 Soil pH

The pH of a soil has a significant influence on nutrient availability (Tunney et al., 2010). There was a significant interaction between soil type and treatment, but not soil texture, for pH ($p<0.001$). Averaged across all soil types, the addition of unamended slurry led to significant ($p<0.001$) increases in pH compared to soil-only, increasing on average from 5.28 to 5.70 (Table 6.4). In general, soils treated with amended slurry were not significantly different to unamended slurry, but were significantly different ($p<0.001$) to soil-only. The average pH for alum and PAC-treatments were 5.60 and 5.73, respectively. There was a strong correlation between soil pH and WEP, M3-Al, M3-Ca, M3-P, degree of P saturation (DPS) and P_m ($p<0.001$).

6.3.3 Morgan's and Mehlich-3 phosphorus

Chemical amendment did not affect plant available P when averaged across the medium loam (A, B, C, F, K, L, N, O, P and Q) and sandy loam (D, G, M and R) textured soils. However, for all other soil types (clay loam, silt loam, silty clay loam, silt loam), addition of amendment resulted in significantly reduced ($p<0.001$) plant available P, with alum, in general, displaying the greatest reductions. From the farmers' perspective, any reduction in plant available P to below agronomic optima would not be desirable and would have more influence over whether to use an amendment than WEP.

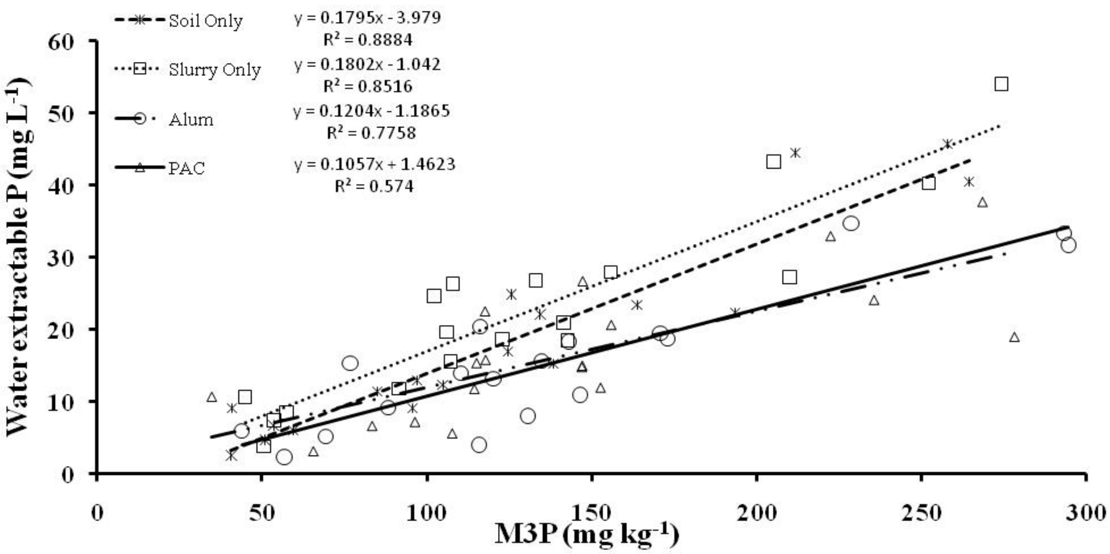
6.3.4 Metals analysis

Overall, there was a strong correlation between M3-Al and WEP, M3-Fe, M3P, DPS, pH and P_m ($p<0.001$); between M3-Fe and WEP, M3-Al, M3P, DPS, M3-Ca and P_m ($p<0.001$); and between M3-Ca and WEP, M3-Fe, pH and P_m ($p<0.001$). Averaged across all soil types, the use of alum-amended slurry led to a significant ($p<0.01$) increase in M3-Al compared to PAC-amended slurry. In general, slurry treatments resulted in significant ($p<0.05$) decreases in M3-Fe compared to soil-only, but addition of either amendment did not lead to significant differences compared to unamended slurry. There were also no observed trends or differences between slurry treatments for M3-Ca, Co, Cu, K, Mg, Mn, and Zn, which indicated that the addition of amendments did not adversely affect the availability of these metals and nutrients to plants.

6.3.5 Relationship between soil water extractable phosphorus and Mehlich-3 phosphorus and degree of phosphorus saturation

There were significant positive relationships between WEP, M3P and DPS for each treatment (Fig. 6.3; $p<0.001$). Slopes for the soil-only and unamended slurry treatments were similar, whilst the alum and PAC treatments were shallower. This indicated that for a given increase in M3P or DPS, the increase in WEP for amended slurry treatments was less compared to the soil-only and unamended slurry treatments. This is in agreement with the fact that, in general, alum and PAC were effective in reducing WEP.

a)



b)

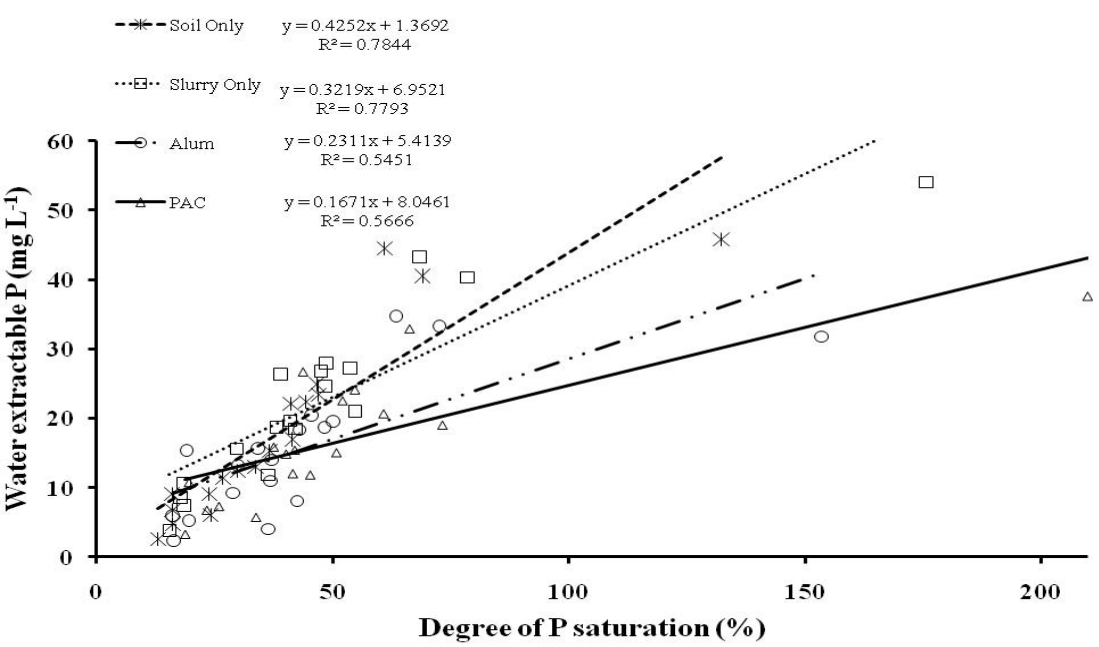


Figure 6.4 Water extractable P (mg L^{-1}) versus M3P (mg kg^{-1}) a), and versus degree of P saturation (%) b).

6.4 Conclusions

The addition of slurry increased soil WEP across all soil types examined in this study. The addition of alum and PAC resulted in reductions of soil WEP ranging from 16% to 48% and

0.2% to 40%, respectively. The efficacy of the amendments depended on the initial soil STP and DPS, which indicated the importance of identifying appropriate amendments for the diverse range of soil types and their P status that may be present on a farm. Due to their high cost, the incorporation of amendments into existing management practices could only be justified in a targeted manner in areas such as CSAs, which have a high risk of P loss. However, if chemical amendment becomes a more common practice, then the associated cost of employing it as a mitigation measure may become more economical for farmers. This is important in gaining acceptance among farmers for implementation. The amendments examined did not adversely affect the availability of Ca, Co, Cu, K, Mg, Mn and Zn to plants. From the studies carried out by the authors to date, PAC appears to be the most ideal amendment with which to chemically amend pig slurry. Future research must examine at field and catchment-scale over a range of soil types, how amendments affect nutrient balances under real-life conditions which cannot be replicated in laboratory testing.

6.5 Acknowledgements

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Chapter 7
Conclusions and Recommendations

7.1 Overview and context

Increased intensification of pig farming activities, legislation reducing the amount of land onto which pig farmers may apply slurry, along with more stringent water quality targets (e.g. the Water Framework Directive, 2000/60/EC; EC, 2000), 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 of disposing of pig slurry. However, as the pig industry is concentrated in specific areas of Ireland, lands surrounding pig farms may not be appropriate for landspreading. Transportation of pig slurry to other, more appropriate, land is not currently a viable option, as transportation costs are prohibitive. In certain instances, pig slurry may have to be applied to land which is at, or approaching, maximum capacity for slurry application. This could be potentially problematic from environmental and legislative perspectives, particularly if the land is located in a critical source area (CSA), which is potentially more likely to trigger eutrophication of receiving waters. A potential solution to this problem is the chemical amendment of pig slurry prior to land application in CSAs. This type of targeted use of chemical amendments could allow the land application of pig slurry in certain circumstances, while reducing the potential for surface runoff and leaching of nutrients and suspended solids (SS).

7.2 Conclusions

This work has shown that poly-aluminium chloride (PAC) appears to be the most suitable amendment with which to chemically amend pig slurry. Whilst alum resulted in greater reductions of soil water extractable phosphorus (WEP) than PAC, it also incurred greater reductions in plant available phosphorus (Chapter 6). Poly-aluminium chloride performed best in overall removal of runoff P and SS (Chapters 3 and 4), although each of these studies was only carried out on one soil type. There was little difference between leachate and greenhouse gas (GHG) emissions from alum and PAC-amended slurry (Chapter 5). Costs are comparable (Chapter 2), 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 runoff studies conducted where slurry was landspread without incorporation, chemical amendment significantly reduced all types of runoff P losses, but not to below those of soil-only. This indicates that although incidental losses may be reduced by the chemical amendment of pig slurry, soils of a high STP may still pose an environmental danger of chronic P losses. At time intervals of less than 48 h, runoff P losses from amended slurry were less than those from unamended slurry, indicating that chemical amendment may be more effective at reducing P losses than current time interval-based legislation. The high runoff P losses from unamended slurry at time intervals of less than 48 h after slurry application, combined with the large decrease of P losses within this time frame, confirm that the prohibition of land-spreading slurry if heavy rain is forecast in the subsequent 48 h (S.I. No. 610 of 2010) is justified. As well as reducing P losses in runoff, ferric chloride ($FeCl_3$) and PAC also reduced SS losses to below that of the soil-only, and even to below 35 mg L^{-1}, the treatment standard necessary for discharge to receiving waters. There are no limits for the levels of aluminium in surface water intended for the abstraction of drinking water, but runoff levels of iron were well below the limit of 0.3 mg L^{-1}.

As there are significant costs associated with the use of these amendments, they should only be used strategically in areas with high mobilisation potential, soil test P (STP), degree of P saturation and hydrological transfer potential to surface water, i.e. CSAs, and towards the end of the open period for slurry spreading when unpredictable weather conditions would normally prohibit such operations. As land surrounding pig farms tends to have high STP, the use of amendments may be necessary. Chemical amendment has also been used in the poultry and dairy industries, but may also have the potential to be used in the treatment of wastes from other agricultural industries and the sludge from wastewater treatment. If chemical amendment becomes a more common practice, then the cost associated with its use as a mitigation measure may decrease, making it an even more attractive and economic option for farmers, which is an important aspect in its implementation. The tightening of environmental legislation will also justify investment in P mitigation measures such as chemical amendment.

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

This work has shown that chemical amendment can reduce P in runoff, without any negative impact on nutrient leaching, reactive nitrogen (N) emissions, or soil carbon cycling. This demonstrates that it may be an option for the pig farming industry to allow the land application of pig slurry in certain circumstances, whilst reducing the potential for surface runoff of nutrients to waterbodies, so as to meet the water quality requirements of the WFD. It also illustrated that chemical amendment posed no significant change to GHG emissions from pig slurry, and in the cases of alum and PAC, reduced cumulative nitrous oxide and carbon dioxide losses.

The main conclusions of the study are:

1. Incidental losses of P may be reduced by the chemical amendment of pig slurry; however, soils of a high STP may still pose an environmental danger of chronic P losses.

2. Chemical amendment may be more effective than current time interval-based legislation.

3. Poly-aluminium chloride appears to be the most suitable amendment with which to chemically amend pig slurry.

4. Amendments should only be used strategically in CSAs, and towards the end of the open period for slurry spreading when unpredictable weather conditions would normally prohibit such operations.

5. Before landspreading chemically amended pig slurry, each individual soil type present must be assessed for its suitability.

6. Chemically amending land applied pig slurry is possible without any negative impact on nutrient leaching, soil properties, or GHG emissions.

7.3 Future work and recommendations

1. Although encouraging, chemical amendment of pig slurry must be validated at field and catchment-scale (over a wide variety of soil types) under real life conditions which cannot be replicated at laboratory-scale, and take account factors such as varying and extreme weather conditions, flow dynamics and the presence of a watertable. Long-term testing must monitor runoff and leachate P and N, soil microbiology and 'pollution swapping', including ammonia volatilisation. The effect of incorporating chemically amended slurry must also be examined.

2. Whilst the current study has shown that once-off landspreading of chemically amended pig slurry may be possible without any adverse effects on surface runoff, subsurface leachate, GHG emissions and soil chemistry, future work must examine the long-term effects of repeated land application of chemically amended pig slurry, and the effects, if any, on flora and fauna present in areas on which chemically amended slurry is spread.

3. Future work must investigate the long-term stability of metal-to-P bonds formed during the chemical amendment of pig slurry, and whether there is a danger that these bonds may break down in the future, resulting in increased potential of P loss to the environment.

4. There is an inherent difficulty in gaining acceptance for new technologies among the farming community, and so mitigation measures such as chemical amendment of pig slurry may never be widely implemented at farm-scale. It is hoped that there may be economic rewards to incentivise the use of such mitigation measures.

Appendix A

DP Dissolved phosphorus: Phosphorus which passes through a 0.45-µm filter.

DRP Dissolved reactive phosphorus: Phosphorus which passes through a 0.45-µm filter, and is readily analysable without incubation.

DUP Dissolved un-reactive phosphorus: Phosphorus which passes through a 0.45-µm filter, but is not readily analysable without incubation. Calculated by subtracting DRP from TDP.

EPC_0 Equilibrium phosphorus concentration: The point where no net desorption or sorption occurs between a medium and a phosphorus containing solution.

M3-P Mehlich 3 phosphorus: A measure of plant available phosphorus, used more widely in countries other than Ireland.

MRP Molybdate reactive phosphorus: The term has two different meanings: (a) for filtered samples, MRP is equivalent to DRP measurements; (b) for unfiltered samples, MRP is equivalent to DRP plus a fraction of particulate phosphorus which is reactive to the phosphomolybdenum blue method reagents.

Pm Morgan's phosphorus: The national test of soil plant available phosphorus in Ireland.

PP Particulate phosphorus: Phosphorus which does not pass through a 0.45-µm filter. Calculated by subtracting TDP from TP.

SRP Soluble reactive phosphorus: A measurement used by some studies which is identical to DRP.

STP Soil test phosphorus: An interchangeable term with plant available phosphorus, measured in Ireland as Morgan's phosphorus.

TDP Total dissolved phosphorus: Phosphorus which passes through a 0.45-µm filter, measured by analysing after incubation.

TP Total phosphorus: All phosphorus present in a sample, both dissolved and particulate. Measured by incubating and analysing.

WEP Water extractable phosphorus: An environmental indicator of potential phosphorus loss in runoff.

Appendix B

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Cornelius J. O' Flynn[1]
Owen Fenton[2]
Mark G. Healy[1]

[1]Civil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of Ireland

[2]Teagasc, Johnstown Castle, Environmental Research Centre, Co Wexford, Rep. of Ireland

Research Article

Evaluation of Amendments to Control Phosphorus Losses in Runoff from Pig Slurry Applications to Land

If spread in excess of crop requirements, incidental phosphorus (P) losses from agriculture can lead to eutrophication of receiving waters. The use of amendments in targeted areas may help reduce the possibility of surface runoff of nutrients. The aim of this study was to identify amendments which may be effective in reducing incidental dissolved reactive phosphorus (DRP) losses in surface runoff from land applied pig slurry. For this purpose, the DRP losses under simulated conditions across the surface of intact grassland soil cores, loaded with unamended and amended slurry at a rate equivalent to 19 kg P ha^{-1}, were determined over a 30 h period. The effectiveness of the amendments at reducing DRP in overlying water were (in decreasing order): alum (86%), flue gas desulfurization by-product (FGD) (74%), poly-aluminum (Al) chloride (PAC) (73%), ferric chloride (71%), fly ash (58%), and lime (54%). FGD was the most costly of all the treatments (€7.64/m^3 for 74% removal). Ranked in terms of feasibility, which takes into account effectiveness, cost, and other potential impediments to use, they were: alum, ferric chloride, PAC, fly ash, lime, and FGD.

Keywords: Agitator test; Dissolved reactive phosphorus; Land application; Pig slurry

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1 Introduction

The application of slurry in excess of crop requirements can give rise to elevated soil test phosphorus (P) concentrations, which may take years-to-decades to be reduced to agronomically optimum levels [1]. In addition, it can lead to eutrophication of receiving waters [2]. Phosphorus losses occur in runoff from two sources: (i) "Incidental P losses" take place when a rainfall event occurs shortly after slurry application and before slurry infiltrates the soil, while (ii) "chronic P losses" are a long-term loss of P from soil as a result of a build-up in soil test P caused by application of inorganic fertilizers and manure [1, 3]. The use of amendments may allow the application of manure to soil in intensive farm systems, such as pig farms, while reducing incidental and chronic P losses. This paper proposes a novel and relatively realistic way to identify such amendments.

Alum, aluminum chloride ($AlCl_3$), lime, and ferric chloride are commonly used as coagulants in slurry and wastewater separation operations. Smith et al. [4] found in a field-based study that $AlCl_3$, added at 0.75% of final manure volume to pig slurry, could reduce dissolved reactive phosphorus (DRP) by up to 84%. Smith et al. [5] found that alum and $AlCl_3$, added in a field-based study to pig slurry at 430 mg Al L^{-1}, reduced DRP in runoff water by 84% and DRP in manure by over 99%. In an incubation study, Dou et al. [6] found that technical-grade alum, added to pig slurry at 0.25 kg kg^{-1} of manure dry matter (DM), and flue gas desulfurization by-product (FGD), added at 0.15 kg kg^{-1}, each reduced DRP by 80%. Dao [7] amended stockpiled cattle manure with caliche, alum, and fly ash in an incubation experiment, and reported water extractable P reductions in amended manure compared to the control of 21, 60, and 85%, respectively.

Batch experiments, wherein an amendment and slurry are mixed, are a good way to determine if the addition of a particular amendment is appropriate to reduce P in surface runoff from land applied slurry, but do not account for the interaction between applied slurry and soil, and the effect of infiltration and skin formation on the release of P to surface runoff. An agitator test, wherein an intact soil core, placed in a beaker, is overlain with continuously stirred water [8, 9], enables achievement of batch experiment results, but also simulates the situation in which slurry is applied to soil, allowed to dry, and then subjected to overland flow.

The aim of this study was to: (i) Investigate the effectiveness of various pig slurry amendments to control incidental P losses in runoff applied to permanent grassland, (ii) identify optimum amendment application rates for each amendment, (iii) estimate the cost of each treatment, and (iv) discuss the feasibility of using amendments in a real on-farm scenario.

2 Materials and methods

2.1 Slurry collection and characterization

Pig slurry was taken from an integrated pig unit in Teagasc Research Centre, Moorepark, Fermoy, Co. Cork. 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 entire sample used

Correspondence: Dr. M. G. Healy, Civil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of Ireland
E-mail: mark.healy@nuigalway.ie

Abbreviations: **Al-WTR**, alum-based water treatment residual; **DM**, dry matter; **DRP**, dissolved reactive phosphorus; **FGD**, flue gas desulfurization by-product; **PAC**, poly-aluminum chloride for both the batch study and agitator test was taken as one sample. The slurry was stored in a 25-L drum in a cold room at 11°C prior to testing. The total phosphorus (TP) and total nitrogen (TN) were determined using persulfate digestion. Ammonium-N (NH_4-N) was determined by adding 50 mL of slurry to 1 L of 0.1 M HCl, shaking, filtering through No. 2 Whatman filter paper, and analyzing using a nutrient analyzer (Konelab 20, Thermo Clinical Labsystems, Finland). Slurry pH was determined using a pH probe (WTW, Germany). 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 and internationally are presented in Tab. 1.

2.2 Soil preparation and analysis

Grassed soil samples were collected from a local dry stock farm in Galway, Republic of Ireland. Aluminum (Al) coring rings of 120-mm-height and 100-mm-diameter were used to collect undisturbed soil core samples ($n = 60$). Soil samples ($n = 3$) – taken from upper 100 mm from the same location – were air dried at 40°C for 72 h, crushed to pass a 2-mm sieve, and analyzed for soil test P using Morgan's extracting solution [10]. Soil pH ($n = 3$) was determined using a pH probe and a 2:1 ratio of deionized water-to-soil. The particle size distribution was determined using a sieving and pipette method [11], and the organic content of the soil was determined using the loss of ignition test [12]. The soil used was a poorly drained, sandy loam textured, topsoil (58% sand, 27% silt, and 15% clay) with a soil test P of 16.72 ± 3.58 mg L^{-1}, total potassium 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 Batch study to determine potential amendments

A batch study was carried out to identify appropriate amendments for the agitator test and the rates at which they should be applied to pig manure to reduce water extractable P, an environmental indicator of potential P loss in slurry. The following amendments were added in the batch study: (i) Commercial grade liquid alum (8% Al_2O_3), (ii) commercial-grade liquid poly-aluminum chloride (PAC) (10% Al_2O_3), (iii) commercial-grade liquid ferric chloride (38% $FeCl_3$), (iv) analytical-grade ferric sulfate ($FeSO_4 \cdot 7\ H_2O$),

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 and internationally

Location	Total P (mg L^{-1})	Total N (mg L^{-1})	Total K (mg L^{-1})	NH_4-N (mg L^{-1})	pH	Dry matter (%)	Reference
Ireland	560	2150 ± 212		1248 ± 40	8.9 ± 0.3	3.5 ± 0.2	The present study
	800	4200					S.I. No. 610 of 2010
	1630	6621	2666			5.77	[18] a)
	900 ± 7	4600 ± 21	2600 ± 10			3.2 ± 2.3	[19] a)
Spain	820	3220	1008	1860	7.59	3.2	[20]
USA	707	2037	1412	1366		2	[21]

a) Values changed to mg L^{-1} assuming densities of 1 kg L^{-1}.

Table 2. Characterization of amendments used in the batch and agitator tests (mean ± standard deviation) tests carried out in triplicate

Amendment	Alum	Poly-Al chloride	Ferric chloride	Ferric sulfate	Lime	Fly ash	FGD	Bottom ash	Gypsum	Al-WTR-1	Al-WTR-2
	8% Al_2O_3	10% Al_2O_3	38% $FeCl_3$	$FeSO_4 \cdot 7\ H_2O$	$Ca(OH)_2$					(<2 mm)	(Sludge)
pH	1.25	1.0–3.0				11.2 ± 0.04	8.6 ± 0.0			7.9 ± 0.1	6.9 ± 0.2
WEP (mg kg^{-1})	0					<0.01	<0.01			<0.01	
Al (%)	4.23					5.7 ± 0.2	0.1 ± 0.0	0.42	1.1	11 ± 0.0	5.3 ± 0.2
Ca (%)					54.1	4.9 ± 0.2	20 ± 0.3	0.4	28	1.3 ± 0.1	0.11
Fe (%)	<0.01		38	20		2.2 ± 0.1	0.1 ± 0.0	1.6	0.5	0.2 ± 0.0	0.01
K (%)						0.1	0.03	0.04	0.01	0.03 ± 0.0	<0.01
As (mg kg^{-1})	1	<1.0	<2.8			13 ± 0.6	<0.01			6.2 ± 1.1	<0.01
Cd (mg kg^{-1})	0.21	<0.2	<3.4			0.6 ± 0.0	0.2 ± 0.02	0.28		0.16 ± 0.0	<0.01
Co (mg kg^{-1})						33 ± 1	0.3 ± 0.1	0.43		0.5 ± 0.3	<0.01
Cr (mg kg^{-1})	2.1	<2.0	<48			88 ± 2	3 ± 0.1	14.3		3.8 ± 0.21	0.3 ± 0.02
Cu (mg kg^{-1})			<65			32.7 ± 1.5	37 ± 13	8.1		31.7 ± 1.5	0.6 ± 0.03
Mg (mg kg^{-1})						$12\,200 \pm 610$	2950 ± 58	2120	12 061	165 ± 33	3.2 ± 1.7
Mn (mg kg^{-1})			<1370			347 ± 160	31 ± 0.6	92		79 ± 1	6.9 ± 0.1
Mo (mg kg^{-1})						7.7 ± 0.5	0.73 ± 0.3	0.63		0.47 ± 0.2	<0.01
Na (mg kg^{-1})						1370 ± 610	660 ± 93	859	371	611 ± 180	65 ± 14
Ni (mg kg^{-1})	1.4	<1.0	<48			44 ± 1	11 ± 0.6	9.9		4.8 ± 0.06	0.6 ± 0.2
P (mg kg^{-1})						5460 ± 630	65 ± 20	171	218	234 ± 5.3	18.7 ± 1.6
Pb (mg kg^{-1})	2.8	<2.0	<14			30 ± 2	0.74 ± 0.4	3.9		1.2 ± 0.8	<0.01
V (mg kg^{-1})						155 ± 5	49 ± 2	13.7		3 ± 0.2	0.2 ± 0.01
Zn (mg kg^{-1})						75 ± 31	9.4 ± 2	19.7		17	0.8 ± 0.1
Sb (mg kg^{-1})		<1.0	<2.8								
Se (mg kg^{-1})		<1.0	<2.8								
Hg (mg kg^{-1})		<0.2	<0.7								

WEP, water extractable phosphorus; Al-WTR, alum-based water treatment residual; FGD, flue gas desulfurization by-product.

(v) analytical-grade lime ($Ca(OH)_2$), (vi) fly ash, (vii) FGD, (viii) bottom ash, (ix) gypsum, (x) aluminum-based water treatment residuals (Al-WTR), sieved to <2 mm (Al-WTR-1), and (xi) Al-WTR homogenized sludge (Al-WTR-2). Tests (i–v) were applied based on a metal/TP stoichiometric ratio and (vi–xi) were applied based on a kg kg^{-1} weight basis (slurry DM). The Al-WTR was provided by Galway City Water Treatment Plant. Coal combustion by-products (fly ash, FGD, and bottom ash) were provided by the Electricity Supply Board. The compositions of all the amendments used are shown in Tab. 2.

The pH of the amended slurry was measured after application of amendments at $t = 0$ h. Amendments were added at five different rates to 50 g of slurry and mixed for 10 s. All tests were carried out in triplicate ($n = 3$). At $t = 24$ h, samples were tested for water extractable P after Kleinman et al. [13]. An unamended sample was also used as a study control.

2.4 Agitator test

The agitator test has been used to investigate the release of P from soil [8] and from amended dairy cattle slurry to soil [9]. This experiment replicates the way in which slurry is applied to soil, allowed to dry, and then subjected to overland flow. Although no validation of test results with actual runoff was undertaken, the test provided comparable conditions for assessment of the effectiveness of the amendments at reducing the release of P from land-applied slurry in a realistic way.

In the agitator test, the following treatments were examined in triplicate ($n = 3$) within 21 days of sample collection: (i) A grassed sod-only treatment with no slurry applied, (b) a grassed sod with unamended slurry applied at a rate of 19 kg TP ha^{-1} (control study), and (c) grassed sods receiving amended slurry applied at a rate of 19 kg TP ha^{-1}. Six different amendments (selected from the batch study above) were applied at three different rates (low, medium, and high) based on the results obtained from the batch study. Amendments were added to slurry in a 100 mL plastic cup and mixed for 10 s. Prior to the start of the agitator test, the intact soil samples – at approximately field capacity – were taken from their sampling cores and cut to a height of 45 mm; this was considered sufficient to include the full depth of influence on release of P to overland flow [8]. They were then transferred into 1 L glass beakers. The slurry and amended slurry was then applied to the soil cores ($t = 0$ h) and left to interact for 24 h prior to the sample being saturated. At $t = 24$ h, the samples were gently saturated by adding deionized water to the soil at intermittent time intervals over 24 h until water pooled on the surface. Immediately after saturation ($t = 48$ h), 500 mL of deionized water was added to the beaker. The agitator paddle was lowered to mid-depth in the water overlying the soil sample and the paddle was set to rotate at 20 rpm for 30 h to simulate overland flow (Fig. 1).

Water samples (4 mL) were taken from mid-depth of the water overlying the soil at 0.25, 0.5, 1, 2, 4, 8, 12, 24, and 30 h after the start of each test (i.e., after 500 mL were added). All samples were filtered immediately after sample collection using 0.45-μm filters and prior to being analyzed colorimetrically for DRP using a nutrient analyzer (Konelab 20, Thermo Clinical Labsystems). pH readings were taken in the overlying water at 1 and 30 h after the start of each test.

2.5 Cost

The effects of amendments on slurry viscosity or handling were not considered in the cost analysis. It was assumed that amendments would be added upon delivery, so storage cost on site was excluded

Figure 1. The agitator experimental setup.

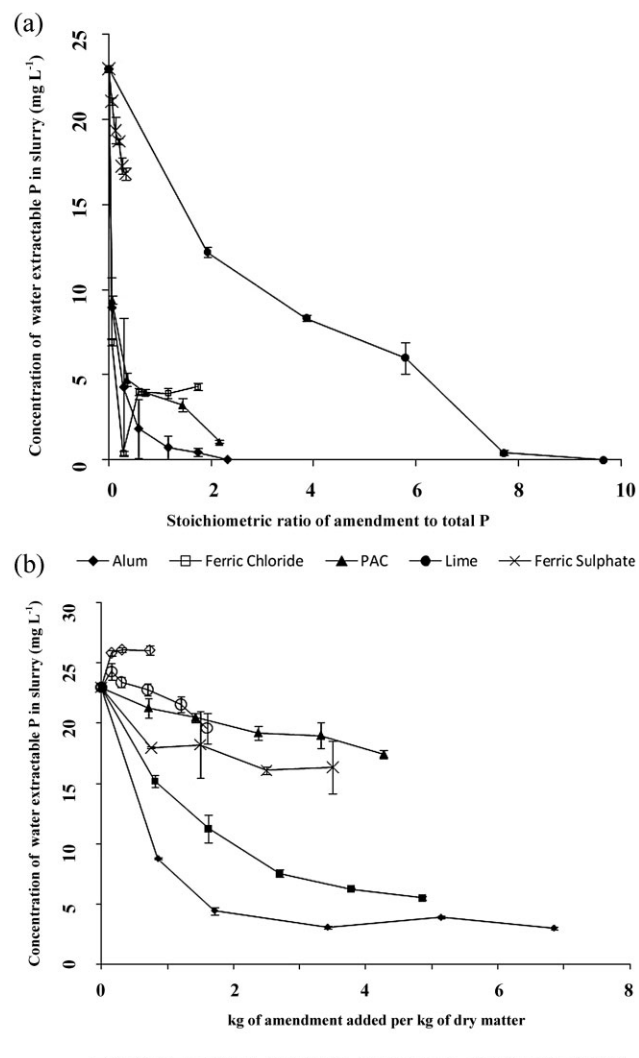

Figure 2. Concentration of water extractable P in pig slurry (mg L^{-1}) as a function of stoichiometric ratio of Al added as alum and PAC, Fe added as ferric chloride and ferric sulfate, and Ca as lime to total P in pig slurry (a), and mass of fly ash, FGD, bottom ash, gypsum, and Al-based water treatment residuals sieved to <2 mm (Al-WTR-1), and homogenized sludge (Al-WTR-2) added per DM of pig slurry (b).

from the analyses. In the case of lime, the cost was estimated using commercial grade lime. The calculated costs took into account the fixed and operational costs for a 75-kW tractor and 2000-gal. splash-plate slurry tanker.

3 Results

3.1 Batch study

The most effective amendments at reducing water extractable P after 24 h were (in decreasing order of effectiveness): Alum (99%), lime (99%), ferric chloride (98%), PAC (95%), fly ash (87%), FGD (76%), gypsum (39%), ferric sulfate (27%), bottom ash (24%), Al-WTR-2 (15%), and Al-WTR-1 (0%) (Fig. 2).

For all solutions, there was a point beyond which further additions of amendments did not significantly reduce water extractable P (Fig. 2). On the basis of inspection of the results, the amendments and their application rates to be used in the agitator test were: (i) Alum (0.29:1, 0.58:1, and 0.88:1 [Al/P]), (ii) PAC (0.18:1, 0.36:1, and 0.72:1 [Al/P]), (iii) ferric chloride (0.34:1, 0.62:1, and 0.89:1 [Fe/P]), (iv) lime (3.86:1, 5.79:1, and 7.79:1 [Ca/P]), (v) fly ash (0.857, 1.71, and 3.43 kg kg^{-1} DM), and (vi) FGD (2.7, 3.78, and 4.86 kg kg^{-1} DM).

3.2 Agitator test

Figure 3 shows the mass of DRP in the overlying water and DRP concentrations over the study duration. The percentage reduction in DRP for each treatment at each rate is shown in Tab. 3. The unamended slurry had a DRP concentration of 17.8 mg L^{-1} in the overlying water. The DRP concentrations in the overlying water, ranked from best to worst, were: Alum, 2.5 mg L^{-1}; FGD, 4.6 mg L^{-1}; PAC, 4.7 mg L^{-1}; ferric chloride, 5.2 mg L^{-1}; fly ash, 7.5 mg L^{-1}; and lime, 8.1 mg L^{-1}. These compare to the water overlying the grassed sod-only treatment, which had a DRP concentration of 2.0 mg L^{-1}.

3.3 Cost

Table 3 shows the estimated cost of addition of amendments and estimations of spreading and agitation costs as a result of their use. In order of increasing cost of use, per m^3 of pig slurry, they are: Ferric chloride (€1.89), fly ash (€2.00), PAC (€2.09), alum (€2.18), lime (€2.84), and FGD (€4.10). Figure 4 shows the total cost of amendment (€ tonne^{-1}) versus percentage reduction in DRP release to overlying water (%) and the reduction in DRP released from soil (kg ha^{-1}). The addition of FGD led to DM contents of above 10%, which would

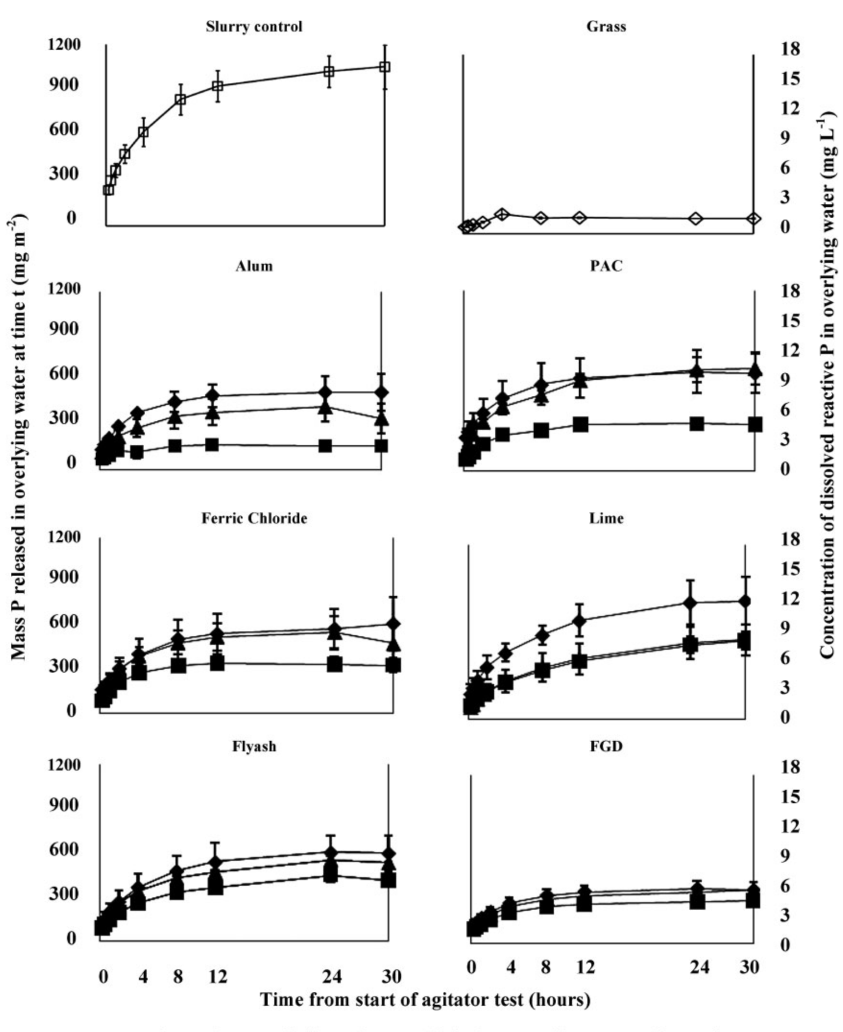

Figure 3. The mass of DRP (mg m^{-2}) and DRP concentration (mg L^{-1}) in water overlying grassed sod-only treatment; grassed sod with unamended slurry; and grassed sod with slurry amended with alum, PAC, ferric chloride, lime, fly ash, and FGD, each applied at three different rates, plotted over the 30 h of the test.

Table 3. Table showing amendments in order of feasibility score, breakdown of costs[a)], cost/m^3 slurry[b)], cost for 500 sow integrated unit, and percentage reduction in DRP in overlying water at 30 h

Amendment[c)]	Feasibility score	Addition rate[d)]	Cost[e)] (€ tonne^{-1})	Rate (kg m^{-3})	Cost of amendment (€ m^{-3})	Spreading (€ m^{-3})	Agitation (€ m^{-3})	Cost water[f)] (€ m^{-3})	Total (€ m^{-3})	500 sow integrated unit[g)] (€ farm^{-1})	DRP Removal (%)	Spreading rate of metal (kg ha^{-1})	Within max. allowable metal spreading rates[h)] (yes/no)
Control					0.00	1.56	0.00	0.00	1.56	16 182	0		
Alum	1	0.29:1 Al/P	150	4	0.58	1.60	0.00	0.00	2.18	22 672	55	5.51	No limit
		0.58:1 Al/P		8	1.16	1.56	0.00	0.00	2.72	28 309	64	11.02	
		0.88:1 Al/P		12	1.76	1.57	0.00	0.00	3.33	34 613	86	16.72	
Ferric chloride	2	0.34:1 Fe/P	250	1	0.34	1.55	0.00	0.00	1.89	19 704	48	6.46	No limit
		0.62:1 Fe/P		2	0.62	1.55	0.00	0.00	2.18	22 655	52	11.78	
		0.89:1 Fe/P		4	0.90	1.56	0.00	0.00	2.45	25 500	71	16.91	
Poly-Al chloride	3	0.18:1 Al/P	280	2	0.53	1.55	0.00	0.00	2.09	21 689	43	3.42	No limit
		0.36:1 Al/P		4	1.07	1.56	0.00	0.00	2.62	27 258	42	6.84	
		0.72:1 Al/P		8	2.13	1.56	0.00	0.00	3.69	38 396	73	13.68	
Fly ash	4	0.030 kg kg^{-1}	14	30	0.40	1.6	0.00	0.00	2.00	20 815	43		Yes
		0.060 kg kg^{-1}		60	0.81	1.64	0.00	0.00	2.45	25 488	48		
		0.120 kg kg^{-1}		120	1.62	1.74	0.00	0.00	3.36	34 910	58		
$Ca(OH)_2$ (Lime)	5	3.86:1 Ca/P	312	4	1.28	1.56	0.00	0.00	2.84	29 511	30	73.34	No limit
		5.79:1 Ca/P		6	1.92	1.56	0.00	0.00	3.48	36 206	53	110.01	
		7.71:1 Ca/P		8	2.56	1.56	0.00	0.00	4.12	42 866	54	146.49	
FGD	6	0.095 kg kg^{-1}	14	95	1.28	1.98	0.43	0.42	4.10	42 634	66		Yes
		0.132 kg kg^{-1}		132	1.79	2.49	0.54	1.09	5.91	61 467	67		
		0.170 kg kg^{-1}		170	2.3	2.98	0.64	1.73	7.64	79 474	74		

DRP, dissolved reactive phosphorus; FGD, flue gas desulfurization by-product.
a) Calculations based on an integrated pig unit with 500 sows, or equivalent stocking rate, indoors for 52 weeks.
b) Slurry properties: total P = 560 mg L^{-1} and 3.5% dry matter (DM).
c) In the case of $Ca(OH)_2$, cost was estimated using commercial grade lime.
d) Addition rates for fly ash and FGD quoted as kg of amendment/kg of slurry.
e) Cost includes delivery of material and addition of material to slurry in storage tank.
f) Addition of some amendments resulted in DM >10%-water addition needed for spreading. In this case, agitation is required for process of adding water.
g) Calculations based on 0.4 m^3 of slurry per sow per week.
h) Max. allowable metal application rates take from S.I. No. 267/2001-Waste Management (Use of Sewage sludge in Agriculture) (Amendment) Regulations, 2001 (www.irishstatutebook.ie).

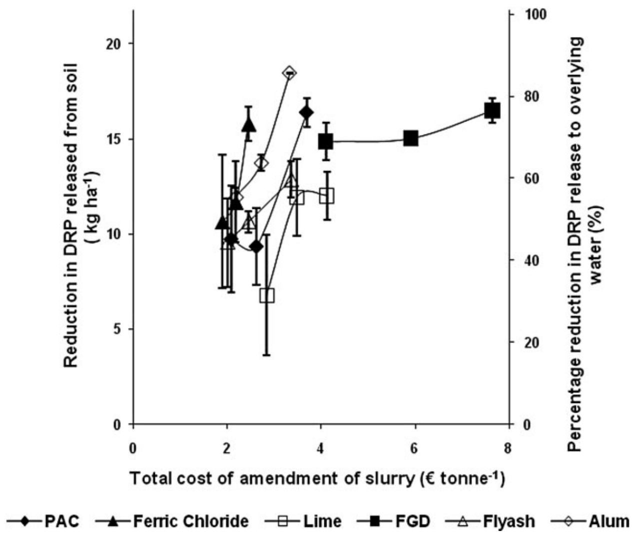

Figure 4. Total cost of amendment (€ tonne^{-1}) of pig slurry plotted against the reduction in DRP lost to overlying water (kg ha^{-1}) and the percentage reduction in DRP release to overlying water from slurry amended with alum, PAC, ferric chloride, lime, fly ash, and FGD, each applied at three different rates.

require water to be added to produce DM of a low enough consistency for slurry spreading operations. Addition of water would require agitation and these, combined with the high volume of addition per m^3, significantly increased the total cost of FGD above the other amendments. Alum, although clearly the best performing amendment, was still competitively priced compared to the other amendments.

4 Discussion

In the batch study, Al-WTR-1 and Al-WTR-2 increased the water extractable P of the slurry when added at some weights. This may be attributable to the fact that there were small quantities of P within Al-WTR-1 and Al-WTR-2 (Tab. 2). There was also P present in fly ash and FGD, but these amendments contained much more calcium (Ca) and magnesium (Mg), which are P sorbing elements. Lime required a much higher stoichiometric addition rate to achieve significant water extractable P reduction, however, this is acceptable as lime is often added to land by farmers and has widespread public acceptance. Ferric sulfate was not tested above a stoichiometric rate of 0.332, as there was a poor response relative to the other amendments at the same addition rate. The reduction in water extractable P compared favorably to that of Dao [7], who reported reductions of 60 and 85% in water extractable P concentrations after adding alum and fly ash, respectively, to stockpiled cattle manure.

Taking into account costs, land application of metals, and potential DRP reductions in overlying water, the amendments, ranked in decreasing order of feasibility, were: Alum, ferric chloride, PAC, fly ash, lime, and FGD.

There was a high initial rise in DRP at the start of each test, with the rate of increase reducing over time toward the end of the study (Fig. 3). It can be seen in almost all cases that the higher the addition rate for each amendment, the lower the peak in DRP concentration. The amendments used in the agitator test all reduced the DRP concentrations in the overlying water. However, they did not reduce the concentrations to below that of the grassed sod-only treatment, which itself was well above 30 μg P L^{-1}, the median phosphate level above which significant deterioration may be seen in river ecosystems [14]. The reason for this is the amendments only reduce the contribution of the slurry to the overlying water DRP and do not affect the contribution of the soil to the overlying water DRP. The reductions in DRP were broadly similar to Smith et al. [5], who achieved reductions in DRP of 84% in runoff water when adding both alum and $AlCl_3$ to pig slurry at 430 mg Al L^{-1} in a field-based study.

The effect of amendments on slurry pH is a potential barrier to their implementation as it affects P sorbing ability [15] and ammonia (NH_3) emissions from slurry [16]. The use of acidifying amendments can lead to increased release of hydrogen sulfide gas (H_2S) from slurry, which is believed to be responsible for human and animal deaths when slurry is being agitated on farms. However, the results from this experiment show the pH of the overlying water not to be significantly affected by the use of amendment.

From the cost analysis, it can be seen that the use of amendments may only be worth pursuing where focused application may be adopted. As legislation allows less slurry to be spread on high P index soils, farmers with these soils have less land available on which to spread slurry. The addition of amendment to pig slurry has the potential to relieve this problem. If a farmer has more than one P index level on a farm, then a way to potentially reduce the cost associated with amending the slurry would be to only amend the slurry that is applied to areas of the farm with a higher soil test P. However, this will only reduce the impact of landspreading on the potential loss of P in runoff and will not impact on the soil test P, which will still be a potential pollution source.

Although, this study did not investigate the release of metals due to the amendment of slurry, previous studies that have found no added risk was posed by amending land applied pig [4] or poultry [17] manure. Moore and Edwards [17] also investigated whether using alum as an amendment affected Al concentrations in the soil or Al uptake by plants. They showed that the use of alum did not negatively affect either. The reason that Al availability was not affected is because Al availability in soils is virtually independent of the level of total Al, but instead is controlled by the geochemical conditions present, with pH being the major influencing factor. Acidic conditions result in the dissolution of clay minerals and Al oxides, causing high concentrations of exchangeable Al. The pH would be expected to increase, which will result in decreased available Al. Moore and Edwards [17] also calculated that it would take up to 400 years of annual application of alum-treated litter to increase the level of total Al in the soil from 7 to 8%, as alum is already the most abundant metal in most soils.

5 Conclusions

The findings of this study are:

(1) All of the amendments trialed in the agitator test have the potential to reduce the release of P in surface runoff from land-applied slurry.
(2) Taking into account costs and land application of metals, suitable amendments which may reduce the risk of surface runoff of P from land applied pig slurry are (in decreasing order of feasibility): Alum, ferric chloride, PAC, fly ash, lime, and FGD.
(3) As there are significant costs associated with the use of these amendments, it is recommended that they are used strategically

in areas which are likely to have potential nutrient loss problems. As land surrounding pig farms tend to have high soil test phosphorus, the use of amendments may be deemed necessary. Although, they reduce the impact of nutrient loss from land application of pig slurry, they do not prevent the loss of nutrients from soil of high nutrient content.

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Appendix C

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

C.J. O'Flynn [a], O. Fenton [b], P. Wilson [c,d], M.G. Healy [a,*]

[a] Civil Engineering, National University of Ireland, Galway, Co. Galway, Ireland
[b] Teagasc, Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland
[c] School of Mathematics and Statistics, University of St. Andrews, Fife, Scotland, United Kingdom
[d] School of Mathematics, Statistics and Applied Mathematics, National University of Ireland, Galway, Co. Galway, Ireland

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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.

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

* Corresponding author. Tel.: +353 91 495364; fax: +353 91 494507.
E-mail address: mark.healy@nuigalway.ie (M.G. Healy).

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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).

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 >8 mg 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 desulfurisation 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, 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 persulphate digestion. Ammonium–N (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 (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 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 0.45 μm filter and analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Filtered (passed through a 0.45 μm 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 persulphate digestion. Particulate phosphorus was calculated by subtracting TDP from TP. Dissolved un-reactive phosphorus (DUP) was calculated by subtracting DRP from TDP. Suspended sediment was tested by vacuum filtration of

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 (mg L^{-1})	TN (mg L^{-1})	TK (mg L^{-1})	NH_4–N (mg L^{-1})	pH (mg L^{-1})	DM (%)	Reference
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 mg kg^{-1}	0.21	<3.4	<0.2
Co mg kg^{-1}			
Cr mg kg^{-1}	2.1	<48	<2.0
Cu mg kg^{-1}		<65	
Mg mg kg^{-1}			
Mn mg kg^{-1}		<1370	
Mo mg kg^{-1}			
Na mg kg^{-1}			
Ni mg kg^{-1}	1.4	<48	<1.0
P mg kg^{-1}			
Pb mg kg^{-1}	2.8	<14	<2.0
V mg kg^{-1}			
Zn mg kg^{-1}			
Sb mg kg^{-1}		<2.8	<1.0
Se mg kg^{-1}		<2.8	<1.0
Hg mg kg^{-1}		<0.7	<0.2

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 neighbouring such a landscape. The high drainage density, high annual rainfall and low annual potential evapotranspiration (20–50% of rainfall) facilitate 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

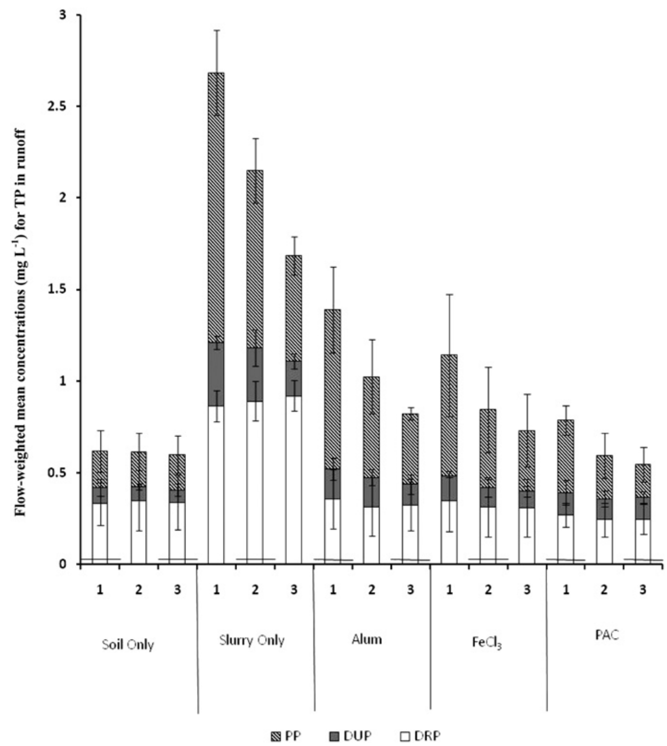

Fig. 1. Histogram of flow-weighted mean concentrations (mg L^{-1}) for dissolved reactive phosphorus (DRP), dissolved unreactive phosphorus (DUP) and particulate phosphorus (PP) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry. Hatched line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

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 RE 1 to 55% during RE 2, and 66% during RE 3. 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

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 ($p < 0.05$).

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.

Fig. 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 (RE 1), and 7 days later (RE 2) 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

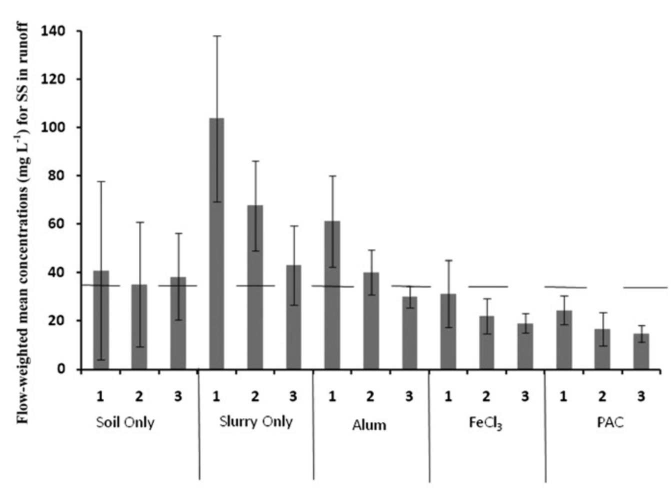

Fig. 2. Histogram of average flow-weighted mean concentration of suspended sediment (SS) (mg L^{-1}) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry. Hatched line = 35 mg L^{-1} standard (S.I. No 419 of 1994).

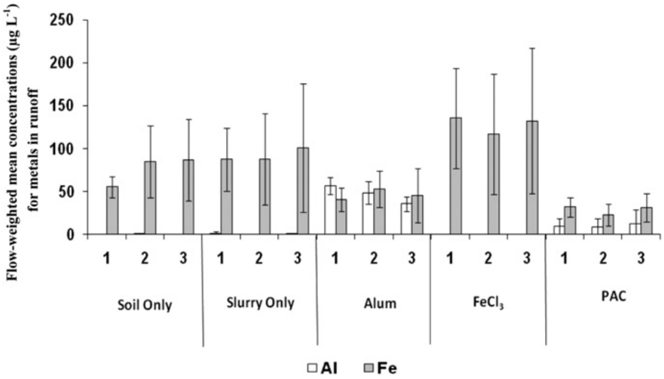

Fig. 3. Histogram of average flow-weighted mean concentration of metals (mg L^{-1}) in runoff at time intervals of 48, 72, and 96 h (denoted as 1, 2 and 3) after land application of pig slurry.

31.1 g ha^{-1} from the slurry control for RE 1 and RE 2 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 Meisinger, 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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Appendix D

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RESEARCH ARTICLE

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

Cornelius J. O' Flynn · Mark G. Healy · Paul Wilson · Nyncke J. Hoekstra · Shane M. Troy · Owen Fenton

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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 water body by prohibiting slurry spreading when heavy rainfall is forecast within 48 h. 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 48 h) between pig slurry application and simulated rainfall with an intensity of 11.0 ± 0.59 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 % 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 (10 % Al_2O_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 48 h 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 12 h were less than from unamended slurry with a TI of 48 h, 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

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C. J. O' Flynn · M. G. Healy (✉)
Civil Engineering, National University of Ireland, Galway, County Galway, Ireland
e-mail: mark.healy@nuigalway.ie

N. J. Hoekstra · O. Fenton
Teagasc, Environmental Research Centre, Johnstown Castle, County Wexford, Ireland

P. Wilson
School of Technology, University of Wolverhampton, Wolverhampton, UK

S. M. Troy
Scottish Rural College, Roslin Institute Building Edinburgh, UK

Introduction

During episodic rainfall events, phosphorus (P) and reactive nitrogen (N_r) fluxes from critical (soil) and incidental (e.g. slurry or fertiliser application) sources can contribute to anthropogenic eutrophication of surface water (Preedy et al. 2001; Kleinman 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; Monteney 2001) has been ratified into national legislation in Ireland and limits the magnitude, timing and placement of inorganic and organic fertiliser 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 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 48 h 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 48 h, which is the limit set by Irish and UK regulations. Assessing the risk of runoff at TIs within these 48 h 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 48 h 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 48-h 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 48 h 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 48 h 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 ($AlCl_3$), lime and ferric chloride ($FeCl_3$) 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 48 h 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 48 h between application and first rainfall event.

Therefore, the aim of this study was to investigate the effect of TI (12, 24 and 48 h) 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 (NH_4^+–N) was determined by adding 50 ml of slurry to 1 L of 0.1 M 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 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.

Pig slurry amendment

Amendments for the present study were chosen based on effectiveness of P sequestration and feasibility criteria (cost

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 (mg L^{-1})	TN (mg L^{-1})	TK (mg L^{-1})	NH_4^+–N (mg L^{-1})	pH (mg L^{-1})	DM (%)	Reference
482±37	3,850±20		2,250±72	7.37±0.07	3.22±0.15	The present study
800	4,200					S.I. No. 610 of 2010
1,630	6,621	2,666			5.77	McCutcheon (1997)[a]
900±7	4,600±21	2,600±10			3.2±2.3	O'Bric (1991)[a]

TP total P, *TN* total N, *TK* total K, *DM* dry matter

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

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 % 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 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 years, 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 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 Standards Institution 1990) and the organic content of the soil was determined using the loss on ignition test (British Standards Institution 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^{-1}, 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 of 203 mg L^{-1}, 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 days 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}. 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 48 h (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 of 0.025 m higher than the grassed sods,

Table 2 Flow-weighted mean concentrations (in milligrams per liter) averaged over three time intervals, application costs per tonne, metal application rate (in kilogram per hectare), and removals (in percent) for dissolved reactive P (DRP), dissolved un-reactive P (DUP), total dissolved P (TDP), particulate P (PP), total P (TP) and suspended solids (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 (%)	Costs (€ $tonne^{-1}$)	Metals (kg ha^{-1})
Soil only	0.10 a	–	0.11 a	–	0.21 a	–	0.14 a	–	0.35 a	–	15.98 a	–	–	–
Slurry only	1.34 b	–	0.60 c	–	1.94 c	–	3.85 c	–	5.78 c	–	377.60 c	–	–	–
Alum	0.21 a	84	0.28 b	53	0.49 b	74	1.78 b	54	2.27 b	61	101.30 b	73	150	16.72[a]
$FeCl_3$	0.21 a	84	0.19 b	69	0.40 b	80	1.48 b	61	1.88 b	67	139.94 b	63	250	16.91[b]
PAC	0.22 a	84	0.26 b	56	0.48 b	75	2.01 b	48	2.49 b	57	135.68 b	64	280	13.68[a]

Means in a column, which do not share a letter, were significantly different (p<0.05)

[a] Spreading rate of Al

[b] Spreading rate of Fe

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, USA) attached to a 4.5 m high metal frame, and calibrated to achieve an intensity of 11.0±0.59 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 dissolved reactive P (DRP) concentration of less than 0.005 mg L^{-1}, a pH of 7.7±0.2 and an electrical conductivity of 0.44 dS m^{-1}. 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 24 h 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 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 μm filter and analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Filtered (passed through a 0.45 μm 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 unreactive 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 μm) filter paper. Prior to filtration, the filter paper was weighed. After filtration, the filter paper was dried at 105 °C for 24 h 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 $FeCl_3$) and three levels of the time factor (12, 24 and 48 h). 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 unreactive 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^{-1} (corresponding to loads of 2.48 and 1.49 mg m^{-2}), 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^{-1} (corresponding to loads of 45.7 and 18.9 mg m^{-2}), respectively, at TI 1 to 3.6 and 1.1 mg L^{-1} (23.5 and 7.5 mg m^{-2}) 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 48 h (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

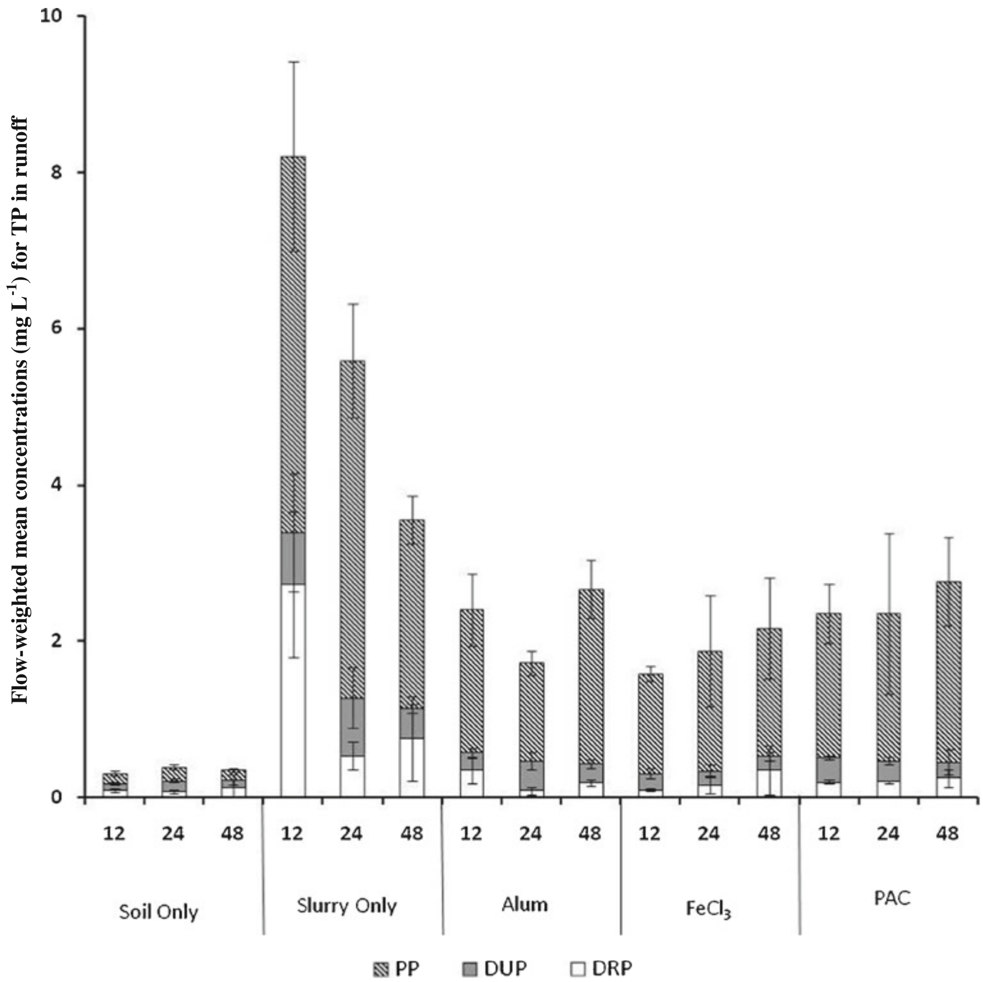

Fig. 1 Histogram of flow-weighted mean concentrations (in milligram per liter) for dissolved reactive phosphorus (DRP), dissolved un-reactive phosphorus (DUP) and particulate phosphorus (PP) in runoff at time intervals of 12, 24 and 48 h after land application of pig slurry

from amended slurry. There was no evidence of any significant interaction between time and treatment type.

Suspended solids and pH in runoff

Loses 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^{-1} (corresponding to loads of 134, 116 and 118 mg m^{-2}) 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^{-1} or 2780 mg m^{-2}). 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^{-1} (European Communities Environmental Objectives 2009, S.I. No. 272), 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 water body that might be expected at field scale.

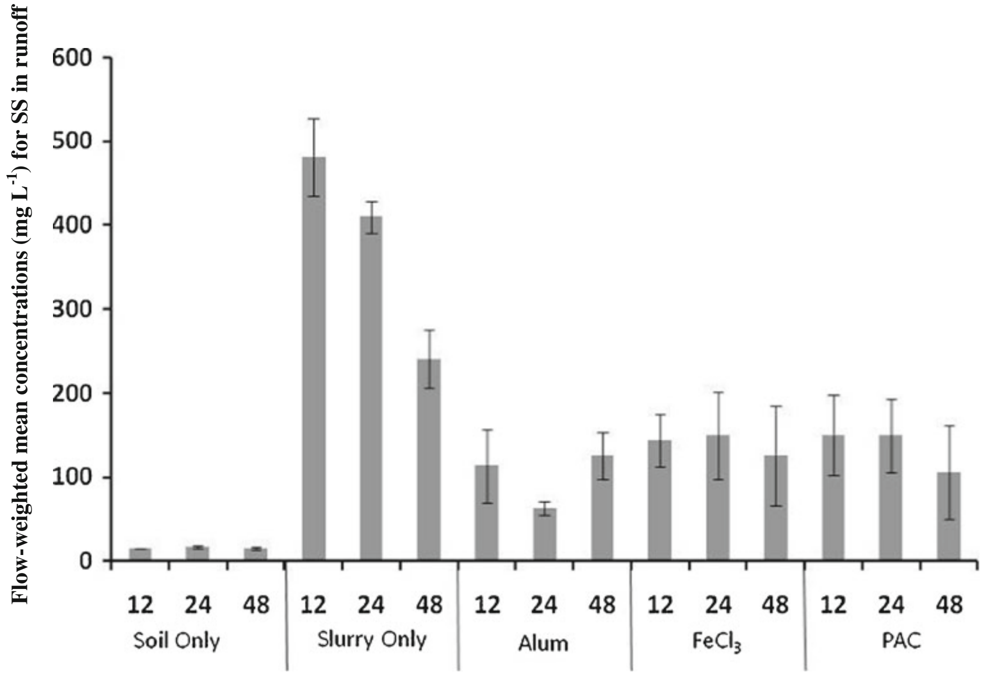

Fig. 2 Histogram of average flow-weighted mean concentration of suspended solids (SS) (milligram per liter) in runoff at time intervals of 12, 24, and 48 h after land application of pig slurry

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^{-1} and found that at 30 min rainfall events, each with an intensity of 100 mm h^{-1}, DRP concentrations in runoff reduced from 8.4 mg DRP L^{-1} at a TI of 1 day to 2.6 mg DRP L^{-1} at a TI of 29 days. Allen and Mallarino (2008) spread pig slurry in a plot study at varying rates up to 108 kg P ha^{-1} and found that during 30-min rainfall events, each with an intensity of 76 mm h^{-1}, DRP and TP loads in runoff were 3.8 and 1.6 times lower at a TI of 10–16 days than at a TI of less than 24 h. 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 24 h after application, and confirms that the prohibition of the land-spreading of slurry, if heavy rain is forecast in the next 48 h (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 $AlCl_3$, 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 $AlCl_3$, 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 $AlCl_3$ 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)

Table 3 Comparison of flow-weighted mean concentrations (milligram per liter) of TP in runoff from two different soils with identical amendments, spreading rates and TIs

	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 (mg L^{-1})	2.8±0.5		16.72±3.58	
Runoff results	TP (mg L^{-1})	Removal (%)	TP (mg L^{-1})	Removal (%)
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
$FeCl_3$	2.17	41	1.14	57

Runoff results are from rainfall events at TIs of 48 h, which occurred in both studies

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 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_3) 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 programme 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 48 h 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 48 h (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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Appendix E

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

Cornelius J. O' Flynn [a], Mark G. Healy [a,*], Gary J. Lanigan [b], Shane M. Troy [c], Cathal Somers [b], Owen Fenton [b]

[a] Civil Engineering, National University of Ireland, Galway, Co., Galway, Ireland
[b] Teagasc, Environmental Research Centre, Johnstown Castle, Co., Wexford, Ireland
[c] Scottish Rural College, Roslin Institute Building, Edinburgh, UK

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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% 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]. 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 N_2O and CO_2 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.

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 (Pm)). 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).

* Corresponding author. Tel.: +353 91 495364; fax: +353 91 494507.
E-mail address: mark.healy@nuigalway.ie (M.G. Healy).

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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,b) 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 (CH_4) from enteric fermentation and manure management and nitrous oxide (N_2O) from N application to soils. The EU 2020 Climate and Energy Package and its associated Effort-Sharing Decision (Decision No 406/2009/EC; EC, 2009) 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,b), 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 1 L of 0.1 M 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,b). 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

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 (mg L^{-1})	TN (mg L^{-1})	TC (mg L^{-1})	NH_4^+-N (mg L^{-1})	pH	DM (%)	Reference
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.
[a] Values 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,b).

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		
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

soil is often of a lower P index and is more suitable for the land-spreading 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 (Pm, 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 (PO_4^{3-}-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 colourimetrically 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):

$$\mathrm{WFPS} = \frac{\mathrm{WC}^{*}\rho_b}{n} \quad (3)$$

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 (NH_4^+-N, NO_3^--N and nitrite-N (NO_2^--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 colourimetrically for DRP, NO_2^-, NH_4^+ and total oxidized nitrogen (TON) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Nitrate was calculated by subtracting NO_2^- 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), Pm, TN and TC. Before analyses, each column was divided into 3 layers (0–0.05 m, 0.05–0.1 m, and 0.1–0.2 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-μm syringe filter, prior to being analysed colourimetrically 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 (0.05–0.1-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 (N_2O, carbon dioxide (CO_2) and CH_4) were analysed 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 tops 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, CO_2 and CH_4 concentrations were analysed using a gas chromatograph (Varian CP 3800 GC, Varian, USA) fitted with a 63Ni electron capture detector (ECD) for N_2O analysis, a thermal conductivity detector (TCD) for CO_2 analysis and a flame ionization detector (FID) for CH_4 analysis. During the analysis, 0.7 mL of a subsample 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 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:

$$\frac{\mathrm{dGas}}{\mathrm{d}t}*10^x*\frac{V_{\mathrm{chamber}}*p*100*\mathrm{MW}}{R*T}*10^y*\frac{1}{A} \tag{4}$$

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 J mol^{-1} K^{-1}; T is temperature in K; 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 mg m^{-2} 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 ± 0.24% (data not shown). Comparatively, at the same time, slurry-only, alum, $FeCl_3$ and PAC treatments had WCs of 31.76 ± 0.44%, 32.45 ± 0.35%, 31.89 ± 0.78%, and 32.13 ± 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,

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 ($p < 0.05$).

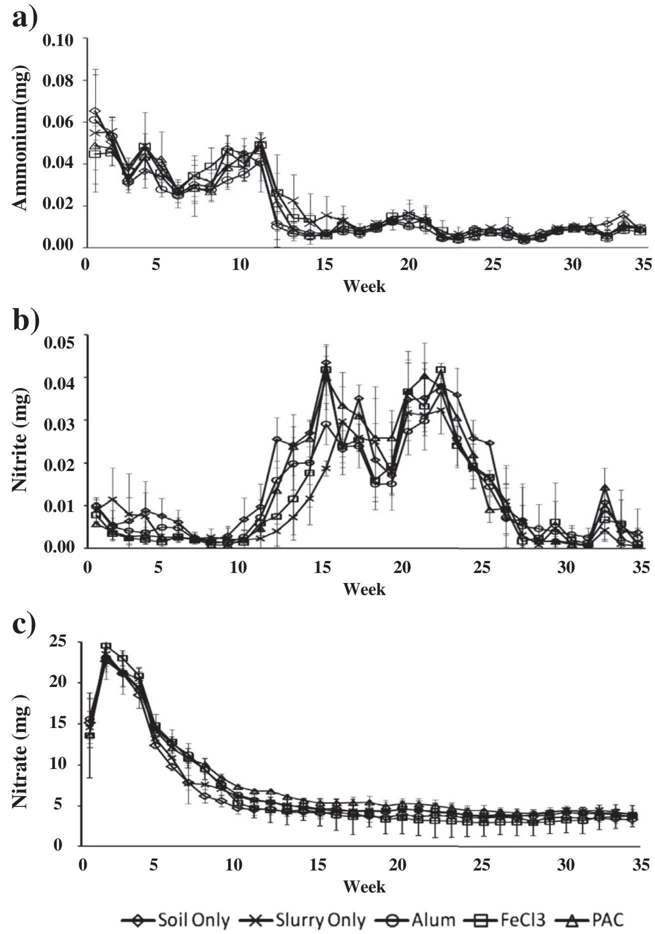

Fig. 1. Average weekly loads of ammonium a), nitrite b) and nitrate c) leached column^{-1} (±standard deviation).

which mainly comprised NO_3^-. The amount of NO_3^- leached increased rapidly until wk 2, before it reduced gradually thereafter (Fig. 1c). 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. 1b).

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 NH_4^+-N kg^{-1} soil, respectively). This compared with values of 44.0 and 48.9 g NH_4^+-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. 2a), with cumulative emissions of 22 ± 8 mg N_2O-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 N_2O-N m^{-2}. The highest cumulative losses of 188 ± 86 mg N_2O-N m^{-2} were 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

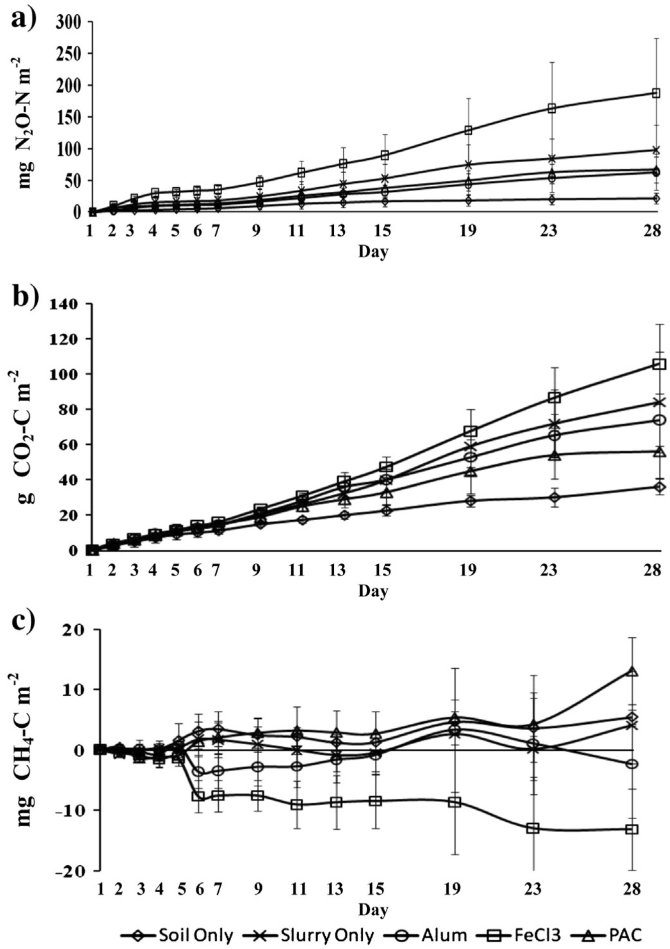

Fig. 2. Cumulative gaseous emissions of N_2O-N a) CO_2-C b) and CH_4-C c) from columns at each sampling period (±standard deviation).

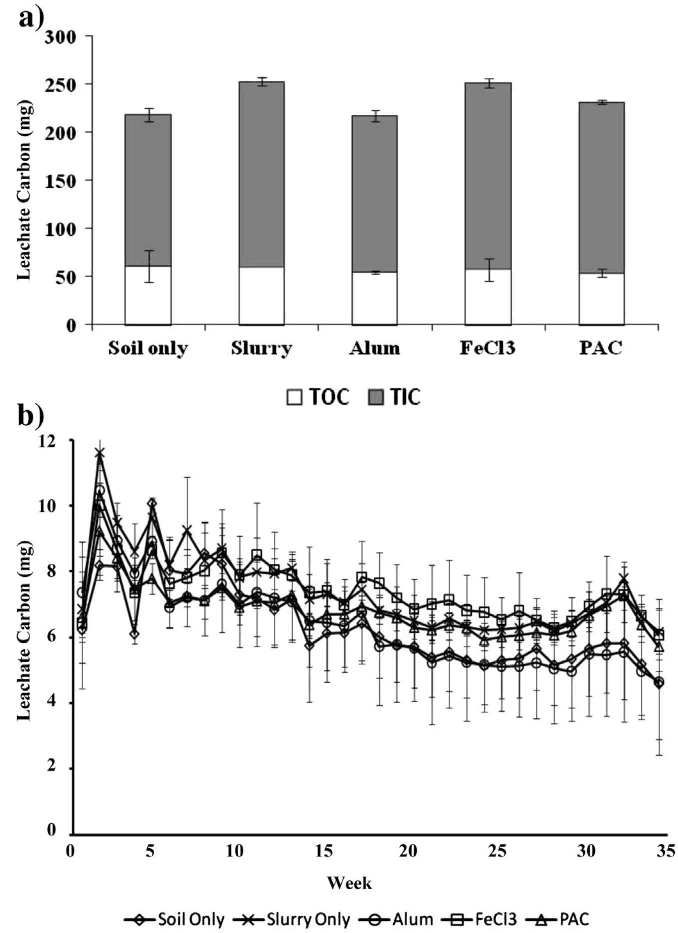

Fig. 3. Cumulative loads of total organic carbon (TOC) and total inorganic carbon (TIC) leached over the duration of the experiment a) and weekly loads of total carbon leached from columns b) (±standard deviation).

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. 3a. 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. 3b); 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 CO_2 followed a similar trend to N_2O emissions (Fig. 2b). The soil-only treatment had the lowest emissions, with cumulative losses of 36 ± 4 g CO_2-C m^{-2}. Losses increased upon application of slurry, but were only statistically significant different ($p = 0.008$) in the case of $FeCl_3$-amended slurry, which had cumulative losses of 106 ± 23 g CO_2-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. 2c), but no treatment had significantly higher losses than the soil-only treatment. After 5 days, all treatments either gained or lost CH_4, with $FeCl_3$-amended slurry acting overall as a net sink with cumulative losses of −13 ± 7 mg CH_4-C m^{-2}, whilst PAC-amended slurry had cumulative losses of 13 ± 6 mg CH_4-C m^{-2}.

4. Discussion

4.1. Nitrogen leachate and soil properties

Denitrification is the mainly microbial reduction of NO_3^--N to the gaseous products nitric oxide (NO), N_2O, or inert di-nitrogen (N_2). 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 NO_3^- 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 NH_4^+ (Fig. 1a). 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 (N_2) and N_2O into the atmosphere (Porporato et al., 2003). Aerobic microbial activity and nitrification is also reduced in these anaerobic conditions where denitrification is facilitated (Porporato 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, 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 (Misselbrook et al., 2005a,b; 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 N_2O after slurry application was as expected (Velthof et al., 2003). The cumulative N_2O 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 NO_3^- 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 N_2O release to the atmosphere (Porporato et al., 2003).

The increase in N_2O emissions associated with $FeCl_3$ addition may be explained as a result of ammonia volatilisation abatement. The difference in soil NH_4^+ 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 $FeCl_3$ 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 ± 0.29 mg L^{-1}) was used in this experiment, its high adsorption capacity for P (0.224 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 CO_2 to the atmosphere. This loss of CO_2 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 CO_2 emissions (Bol et al., 2004; Dumale et al., 2009; Cayuela et al., 2010). The increased CO_2 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, CH_4 emissions are generally of minor importance compared to N_2O emissions (Wulf et al., 2002a,b), as CH_4 emissions from enteric fermentation and during slurry storage are much more important (Chadwick et al., 2000). This is due to CH_4 being produced by decomposition of OM in faecal matter under anaerobic conditions. After landspreading, OM is oxidised to CO_2 and H_2O in the aerobic conditions present. Mineral grassland soils are known to generally be a CH_4 sink, due to either oxidation of CH_4 to CO_2 in soils or incorporation into microbial biomass, with uptake rates ranging from 0.5 to 3.3 mg CH_4 m^{-2} 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 N_2O and CO_2 losses. Moreover, increased N_2O emissions associated with $FeCl_3$ addition were likely to be due to a reduction in ammonia volatilisation, a theory supported by an increase in soil NH_4^+ concentrations.

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