Abstract

This study aimed to quantify leaching losses of nitrogen (N), phosphorus (P) and carbon (C), as well as carbon dioxide (CO₂) and methane (CH₄) emissions from stored slurry, and from packed soil columns surface applied with unamended and chemically amended dairy and pig slurries, and dairy soiled water (DSW). The amendments to the slurries, which were applied individually and together, were: polyaluminum chloride (PAC) and zeolite for pig and dairy slurry, and liquid aluminium sulphate (alum) and zeolite for DSW. Application of pig slurry resulted in the highest total nitrogen (TN) and nitrate-nitrogen (NO₃-N) fluxes (22 and 12 kg ha⁻¹), whereas corresponding fluxes from dairy slurries and DSW were not significantly (p<0.05) higher than those from the control soil. There were no significant (p<0.05) differences in leachate N losses between unamended and amended dairy slurries, unamended and amended pig slurries, and unamended and amended DSW. There were no leachate P losses measured over the experimental duration. Total cumulative organic (TOC) and...
inorganic C (TIC) losses in leachate were highest for unamended dairy slurry (82 and 142 kg ha$^{-1}$), and these were significantly ($p<0.05$) reduced when amended with PAC (38 and 104 kg ha$^{-1}$). The highest average cumulative CO$_2$ emissions for all treatments were measured for pig slurries (680 kg CO$_2$-C ha$^{-1}$) followed by DSW (515 kg CO$_2$-C ha$^{-1}$) and dairy slurries (486 kg CO$_2$-C ha$^{-1}$). The results indicate that pig slurry, either in raw or chemically amended form, poses the greatest environmental threat of leaching losses and gaseous emissions of CO$_2$ and CH$_4$ and, in general, amendment of wastewater with PAC, alum or zeolite, does not mitigate the risk of these losses.

Keywords: Zeolite, chemical amendments, agricultural wastes, leachate, greenhouse gas emissions, soil columns.

1. Introduction

Long term land application of organic fertilizers may result in excessive amounts of nutrients in soil, and may increase the risk of surface and groundwater contamination (Liu et al., 2012; McDowell and Hamilton, 2013; Ulén et al., 2013; Fenton et al., 2017). For example, high nitrate (NO$_3$) concentrations in groundwater used as a drinking water source may lead to environmental (Fenton et al., 2009) as well as human health issues associated with methemoglobinemia (WHO, 2004) and cancer (Camargo and Alonso, 2006; Chiu et al., 2007). Organically derived nitrogen (N), from sources such as manure application, has been shown to be a major contributor to groundwater NO$_3$ concentrations (Baily et al., 2011), while phosphorus (P) leaching to groundwater is associated with eutrophication of associated surface waters (e.g. Qin et al., 2010; Li et al., 2015). This is exacerbated by recent increases in concentrated animal feeding operations, which have led to large volumes of slurries being
generated in relatively small areas and spread at rates that exceed plant nutrient demand (Lee et al., 2007) and where crop production is increased by intensive application of fertilizers and irrigation water (Lin and Chen, 2016).

Landspreading is the most common method of slurry application (Lloyd et al., 2012) and while other methods such as sliding shoe and injection are used to limit N losses through ammonia (NH$_3$) volatization (Sistani et al., 2010), Kayser et al. (2015) concluded that the amount of N input, rather than the method of application, impacts the extent of NO$_3$-N leaching in organic sandy soils. On the other hand, Kleinman et al. (2009) reported that incorporation of dairy manure by tillage reduced P losses in leachate because of the destruction of preferential flow pathways in the soil, while Hodgson et al. (2016) found that shallow injection of dairy slurry to grassland plots resulted in higher and more prolonged survival of faecal indicator organisms than from surface spreading. The partitioning between surface runoff and leaching from land applied agricultural slurries is determined largely by rainfall distribution and intensity, topography, and soil infiltration capacity (Aronsson et al., 2014). Migration of water-borne contaminants through soil is a complex physical and chemical process influenced by factors such as (i) flow characteristics, which depend on the soil structure and grain size (ii) filtration effects due to soil micropores and clogging from applied manure (iv) straining within the organic portion of the applied manure, and (iv) retention of microbes on soil and organic particles by adsorption and adhesion (Unc and Goss, 2004).

Agriculture contributes globally 10-12% of anthropogenic greenhouse gas (GHG) emissions (IPCC, 2007) and land applied organic manures contribute substantially to
this (e.g. Rodhe et al., 2015) through the release of carbon dioxide (CO$_2$), methane (CH$_4$) and nitrous oxide (N$_2$O) from carbon (C) and N compounds in the manures and also, indirectly, by affecting soil properties which can increase GHG emissions from soils (Thangarajan et al., 2013). For example, Huang et al. (2004) reported that manures with high C:N ratios may reduce CO$_2$ emissions and increase soil organic carbon, while manures with low C:N ratios may lead to an increase in soil CO$_2$ emissions. Emissions of CH$_4$, which is generated under anaerobic conditions, tend to be limited from slurries applied to well aerated soils; however, slurry storage emissions can be substantial and can exceed those from landspreading (Rodhe et al., 2015). Currently in many countries, abatement of such emissions during storage is seen as a cost effective measure to meet national emission targets.

The use of disturbed soil columns to measure leaching and transport of contaminants through soils is a well-established laboratory method (e.g. Jin et al., 1997; Enell et al., 2004; Dontsova et al., 2006) and while macropore structure of intact soils is disturbed during the repacking process (McLay et al., 1992), soil columns nevertheless facilitate the investigation of contaminant transport in a homogenous soil under controlled conditions (Murphy, 2007). Previous studies have examined the potential of slurry amendments to mitigate leachate losses and GHG emissions from land applied pig and dairy slurries (O’Flynn et al., 2013; Brennan et al., 2015), but currently there are no data available to evaluate and compare the effectiveness of zeolite used in combination with chemical amendments to mitigate leaching losses of N, P and C, and emissions of CO$_2$ and CH$_4$ (in storage and upon application to land) when applied to dairy and pig slurries and dairy soiled water (DSW). Therefore, the objective of this laboratory-based study was to investigate if zeolite and either poly-aluminium
chloride (PAC) or alum amendments, applied to dairy and pig slurries and to DSW at rates previously investigated to mitigate N, P and suspended solids (SS) losses from grassed soil in rainfall simulation studies (Murnane et al., 2015) and surface applied to repacked grassland soil columns, were also effective in reducing (i) leached N, P and C losses over a 7 month experimental period and (ii) CO₂ and CH₄ emissions over a 28 day experimental period.

2. Materials and Methods

2.1 Soil

2.1.1 Sampling and Analysis

Soil samples were taken from the top 0.2 m of a 0.863 ha grass (perennial ryegrass, tyrella diploid [Lolium perenne L.]) plot at the Teagasc Agricultural Research Centre, Moorepark, Fermoy, Co. Cork, Ireland and immediately transported to the laboratory. The plot had been grazed by dairy cows and received c. 200 to 250 kg N ha⁻¹ annually, but no P application, for > 5 yr prior to soil sampling. The soil, which had a loam texture, was air dried for ten days, ground to pass a 2 mm sieve and mixed thoroughly to provide homogenous sub-samples at the laboratory. The particle size distribution was determined by hydrometer analysis (ASTM F1632) and organic matter content by weight loss-on-ignition (Sims and Wolf, 1995). Soil total carbon (TC) and total nitrogen (TN) were determined by high temperature combustion (McGeehan and Naylor, 1988) and pH using a soil to distilled water ratio of 2:1. Soil samples were extracted with Mehlich III solution (Mehlich, 1984) and extract P, potassium (K), calcium (Ca), magnesium (Mg) and aluminium (Al) were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Cation exchange capacity (CEC) was determined from Mehlich III analyses by the sum of
cations (Ross, 1995). Water soluble organic C (WSOC) was determined by shaking 5 g of dried soil with 50 mL of distilled water for 30 min \( (n=3) \) and measuring the total organic C (TOC) of the filtered \((0.45 \mu m)\) supernatant \( (BS\ EN\ 1484) \) (BSI, 1997) using a BioTector analyzer (BioTector Analytical Systems Ltd). Soil water extractable phosphorus (WEP) was determined by shaking 5 g of dried soil with 25 mL of distilled water for 30 min \( (n=3) \) and testing the filtered \((0.45 \mu m)\) supernatant colorimetrically using a nutrient analyser (Konelab 20, Thermo Clinical Laboratories Systems, Finland).

2.1.2 Batch Studies

The ability of the soil to adsorb P (measured as dissolved reactive phosphorus, DRP) was investigated in batch experiments by adding 90 mL of varying concentrations \( (2 – 175 \text{ mg P L}^{-1}) \) of synthetic wastewater to flasks containing 5 g soil \( (n=3) \). All samples were shaken on a reciprocating shaker for 24 h at 250 excursions per minute (epm) and on removal, were allowed to settle for 1 h, filtered through a 0.45 \( \mu m \) filter, and tested colorimetrically using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). The data were then modelled using a Langmuir isotherm to establish the maximum soil P-adsorption capacity.

2.2 Agricultural slurries

Three types of agricultural wastes (dairy slurry, pig slurry and DSW) were collected in 25 L containers from the Teagasc Agricultural Research Centre, Moorepark, Fermoy, Co. Cork. All slurries were homogenized immediately prior to collection and transferred directly to a temperature-controlled room \((10.9\pm0.7 ^\circ C)\) in the laboratory. All slurry samples were tested within 24 h of collection \( (n=3) \) for TOC and total
inorganic carbon (TIC) (BS EN 1484, 1997) and for TN by combustion oxidation followed by spectrophotometry using a BioTector analyzer. Total phosphorus (TP) was measured using acid persulfate digestion and dry matter (DM) was measured by drying at 105 °C for 24 h. Dissolved reactive P was measured colorimetrically using filtered (0.45 µm) subsamples. Ammonium (NH$_4$-N) was extracted by shaking 10 g of fresh waste in 200 mL of 0.1M HCL on a peripheral shaker for 30 min at 200 rpm, centrifuging at 17,970 RCF for 5 min and measuring colorimetrically. All parameters were tested in accordance with the standard methods (APHA, 2005).

### 2.3 Slurry amendments

The results of a laboratory runoff study by Murnane et al. (2015) determined the optimum combined chemical and zeolite application rates for reductions in NH$_4$-N and DRP, and these were used in the current study. The applied chemical and zeolite amendments were based on TP concentrations and DM content of the slurries, respectively. The chemical amendments applied were commercial grade liquid PAC (10% Al$_2$O$_3$) added to the dairy and pig slurries at rates equivalent to 12.8 and 3.8 kg t$^{-1}$ (0.42 and 0.15 mg per column), and commercial grade liquid aluminum sulfate (alum) (8% Al$_2$O$_3$) added to the DSW at a rate equivalent to 1.0 kg t$^{-1}$ (0.04 mg per column). Turkish zeolite (clinoptilolite), comprising 66.7% SiO$_2$ and 10.4% Al$_2$O$_3$, was sieved to 2.36 – 3.35 mm and added at rates equivalent to 202, 133, and 28 kg t$^{-1}$ (6.7, 5.2 and 1.2 g per column) to the dairy and pig slurries and DSW, respectively. All amendments were added to the slurries in 100 mL containers and mixed thoroughly for approximately 1 min before applying immediately by hand to the soil surface.
2.4 Column setup

Thirty uPVC columns, each with internal diameter of 10 cm and depth of 30 cm, were placed on a timber support frame and located in a temperature-controlled room for 7 months at 10.5±0.5 °C and relative humidity of 89.5±4.0 % (representative of the average temperature and humidity in Ireland). In order to ensure free draining soil conditions, each column was fitted with a perforated end cap at the base above which a 5 cm layer of 5-10 mm graded gravel was placed to prevent washout of the soil. The columns were then filled in 5 cm layers to a compacted (ρ_{bulk} = 1.06 g cm^{-3}) depth of 20 cm with sieved soil (<2 mm), which had been pre-mixed with distilled water to a moisture content of approximately 33%, matching *in situ* field conditions. At each layer, soil was pressed against the column wall to avoid preferential flow through the column and the surface of each layer was lightly scarified after compaction and before addition of the next layer to ensure hydraulic connectivity between layers (Plummer et al., 2004).

Each column was irrigated with 160 mL of distilled water (simulating rainfall), applied twice weekly in two 80 mL increments over a 2 h period (representative of a 6-month, 2-h rainfall event) and was equivalent to an annual average rainfall of 980 mm. Drainage water leachate was collected weekly in containers at the base of the columns (Figure 1). Following an acclimatization period (9 wk) to achieve steady-state soil conditions, unamended and unamended slurries were surface applied to the columns on week 10. The treatments (n=3) examined were (i) soil only (no slurry) (ii) unamended dairy and pig slurries and DSW (iii) PAC-amended dairy and pig slurries, and alum-amended DSW, and (iv) PAC and zeolite-amended dairy and pig slurries, and alum and zeolite-amended DSW. The slurry applications rates, net of
amendments, were equivalent to 39, 46 and 50 t ha\(^{-1}\) (33, 39 and 42 g per column) for dairy and pig slurries and DSW. These rates were the maximum permissible based on limits of 21 kg P ha\(^{-1}\) for dairy slurry, 170 kg N ha\(^{-1}\) for pig slurry, and a volumetric limit of 50 m\(^3\) ha\(^{-1}\) for DSW (SI No. 31, 2014). Irrigation of the columns with distilled water and leachate collection after slurry application continued at the same rate for the full duration of the experiment.

2.5 Leachate analysis

Composite leachate sub-samples were filtered through 0.45 µm filters and measured for (i) DRP, NH\(_4\)-N, total oxidized nitrogen (TON) and nitrite-N (NO\(_2\)–N) using a nutrient analyzer (Konelab 20, Thermo Clinical Labsystems, Finland) (ii) total dissolved nitrogen (TN\(_d\)) and dissolved organic and inorganic C (DOC and DIC) using a BioTector Analyzer, and (iii) total dissolved phosphorus (TDP) using acid persulphate digestion. Unfiltered sub-samples were tested for (i) TN, TOC and TIC using a BioTector Analyzer (ii) TP using acid persulphate digestion, and (iii) pH (WTW pH probe, Weilheim, Germany). Calculated parameters were (i) nitrate-N by subtracting NO\(_2\)–N from TON (ii) particulate nitrogen (PN) by subtracting TN\(_d\) from TN (iii) organic N (N\(_{org}\)) by subtracting TON + NH\(_4\)-N from TN (iv) dissolved organic nitrogen (DON) by subtracting TON + NH\(_4\)-N from TN\(_d\) (v) dissolved unreactive phosphorus (DUP) by subtracting DRP from TDP, and (vi) particulate phosphorus (PP) by subtracting TDP from TP.

2.6 Gas sampling and analysis

An Agilent 7890A Gas Chromatograph (Agilent Technologies Inc., California, USA) was used to analyse gas samples. All injections were made in the direct mode using a
1 mL sample loop with injection temperature set to 100 °C. The oven temperature was set to 60 °C with a post run time of two minutes at 110 °C. The N₂ carrier gas was supplied at a rate of 21 mL min⁻¹. Gas samples were collected from each column in accordance with Parkin and Venterea (2010) on day 1 (day of slurry applications) and subsequently on days 2, 3, 4, 5, 6, 7, 8, 12, 14, 18, 22 and 28. Raw untreated samples (n=3) of dairy and pig slurries and DSW were also stored in separate columns, from which gas samples were collected on days 1, 2, 3, 7, 9, 13, 17, 24, 31, 38 and 52. A static headspace (0.1 m deep) was formed by sealing the top of each column with a rubber stopper (t = 0 min) and gas samples (7 mL) were withdrawn at 0, 5, 10 and 20 min via a rubber septum placed at the side of the column half way down the headspace (Figure 1). Each sample was injected into a pre-evacuated 6-mL screw cap septum vial and the rubber stoppers were removed after gas collection. On days when gas collection coincided with irrigation of the columns (days 5, 8 and 12), samples were taken 1 h after water application.

All samples were measured for CO₂ and CH₄ and the data were analysed by calculating the rate of change of CO₂ and CH₄ concentrations in the chamber headspace using linear regression. Fluxes (g m⁻² h⁻¹) were calculated (Troy et al., 2013) as:

\[
\text{Flux} = \frac{\Delta \text{Gas} \times V_{\text{headspace}} \times \rho_{\text{gas}}}{100 \times \Delta t \times A_{\text{column}}} \tag{1}
\]

where: \( \Delta \text{Gas} / \Delta t = \) rate of change of gas concentration (% h⁻¹); \( V_{\text{headspace}} = \) headspace volume (m³); \( \rho_{\text{gas}} = \) gas density at operating temperature (g m⁻³), and \( A_{\text{column}} = \) column surface area (m²). Negative fluxes indicated gas uptake within the column, while
positive fluxes indicated gas emissions. Cumulative fluxes were determined by multiplying each gas flux by the time interval between sampling.

2.7 Data analysis

Prior to analysis, all data were tested for normality and homogeneity of variance to ensure compliance with Gaussian distribution requirements. Differences in leachate flux and gas emissions were assessed using one-way ANOVA in SPSS (IBM SPSS Statistics 20 Core System). Statistical results were considered significant at $\alpha = 0.05$ and all differences discussed in the text are at this significance level.

To identify the treatments that had the potential to cause the most environmental damage in terms of GHG emissions and leaching of nutrients and carbon, the cumulative TN and TC losses (kg ha$^{-1}$) and the cumulative CO$_2$ and CH$_4$ losses (expressed as total equivalent CO$_2$ emissions in kg CO$_2$-C ha$^{-1}$) over the study duration were added together (after Healy et al., 2014). Although this method does not take into account legislative drivers which may emphasise potential groundwater impact over gaseous emissions in some countries, it serves to contextualise the study results and allows overall impact of each treatment to be estimated and compared to one another.

3 Results and Discussion

3.1 Soil and slurry classification

The physical and chemical characteristics of the soil are shown in Table 1. The soil was classified as a well graded slightly acidic (pH 5.99±0.20) loam with a relatively low C:N ratio (8.65±0.25) and a high Ca:Mg ratio (11.7) indicating deficient Mg.
concentrations (Eckert, 1987), and low soil water extractable P (<5 mg kg\(^{-1}\)). The maximum measured soil P adsorption capacity was 518 mg P kg\(^{-1}\) soil (Figure S1). The characterizations of the three agricultural wastes are shown in Table 2. The concentrations of TN in dairy slurry (1,158±24 mg L\(^{-1}\)) and TP in pig slurry (199±3 mg L\(^{-1}\)) were slightly lower than those used in similar type studies (e.g. O’Flynn et al., 2013; Brennan et al., 2015), but overall the compositions of the slurries were within the range of expected values (Scotford et al., 1998; Martinez-Suller, 2010).

3.2 Leachate flow, phosphorus and pH

The weekly average volume of leachate (weeks 10 – 28) collected from all columns following the acclimatization period (weeks 1 – 9) had a high leachate to irrigation ratio (98.1±7.4%) and all columns remained free draining, indicating steady-state flow conditions throughout the experiment. There were no soil P losses measured in the leachate for all treatments, reflecting the very low proportions of P applied in the slurries compared to the net P storage capacity of the soil (1.9, 0.8 and 0.1% for dairy and pig slurries and DSW, respectively). It is likely that the low initial soil P concentration, its high adsorption capacity and the destruction of soil macropore networks in the packed columns (van Es et al., 2004) also contributed to the retention of P in the soil. The absence of P in the leachates reflect the sub-optimal soil C:N:P ratios (Kirkby et al., 2011) and their consequent inhibition on the growth of heterotrophic microorganisms to assimilate C and autrophic nitrifiers to assimilate N from the applied wastes. The average pH of the leachate remained constant for all treatments (8.38±0.16) throughout the study. The interactive effects of PO\(_4\), NH\(_4\) and NO\(_3\) ions can influence the soil adsorption properties and while the coexistence of PO\(_4\) and NO\(_3\) may improve adsorption, separately they are likely to have a negative
effect. The presence of NH₄ however is likely to positively affect soil adsorption 
(Shen at al., 2017).

3.3 Leachate Nitrogen

Total N in the control soil leachate increased (3.6 to 23.8 mg column⁻¹, equivalent to 4 
to 28 kg ha⁻¹) rapidly during the first three weeks of the acclimatization period (weeks 
1 – 9) and then declined steadily in the following six weeks, where it remained 
constant at an average flux of 2.5±1.2 kg ha⁻¹ for the remainder of the experiment. 
This initial increase and subsequent decrease was also observed to occur for NO₃-N in 
the control soil leachate (Figure 2). The effect of wetting dry soil is well known to 
result in short lived pulses of C and N mineralisation (Borken and Matzner, 2009), 
which can exceed those of permanently moist soils and persist for several weeks 
(Beare et al., 2009).

Application of unamended and amended pig slurries in week 10 resulted in increased 
TN fluxes between weeks 14 and 24, peaking between 20 and 22 kg ha⁻¹ for all 
treatments at week 18 (Figure 2 – B1). There were similar increases in NO₃-N during 
the same period, which formed on average 39.4% of TN for all slurries and all 
treatments (Figure 2 – B2). These leaching losses were lower than those reported by 
Bolado-Rodríguez et al. (2010) in a soil column experiment to measure the effect of N 
and TOC leaching from surface applied raw and air stripped pig slurries irrigated with 
CaCl₂ solution at a constant rate equivalent to 1.7 mm h⁻¹ and slightly lower than 
those reported by Troy et al. (2014), who measured peak amounts of NO₃-N in week 
18 equivalent to c. 14 kg ha⁻¹ in leachate from a tillage soil mixed with pig manure 
biochar. The high NO₃-N losses from pig slurry reflect the large proportion (91%) of
mineral N (predominantly NH$_4$-N) in the applied slurry (Table 2), which can be
quickly converted to NO$_3$ and the likely insufficient anoxic zone within the soil
column for denitrification (An et al., 2016).

There were no significant differences between treatments for pig slurries for TN and
between unamended pig slurry and pig slurry amended with zeolite and PAC for NO$_3$-
N in leachate; however, pig slurry amended with PAC had lower cumulative TN and
NO$_3$-N fluxes than unamended pig slurry and pig slurry amended with PAC and
zeolite (Figure 3, Table S1). This is consistent with the findings of O’Flynn et al.
(2013), who also found no significant differences in leachate N and C from
unamended and PAC-amended pig slurries in a soil column experiment. The reduced
cumulative leachate N and NO$_3$-N fluxes from PAC-amended pig slurry may be due,
in part at least, to the flocculation of N-enriched slurry particles on the upper levels of
the soil surface, reducing their migration through the soil. Addition of zeolite to the
pig slurry may also have accelerated organic degradation (Zhang et al., 2016) and
contributed to the mineralisation of N to NH$_4$-N, thereby increasing NO$_3$-N
concentrations in the leachate from the pig slurry amended with zeolite and PAC.

In general, application of unamended and amended dairy slurries did not significantly
increase leachate TN (average 2.7±1.8 kg ha$^{-1}$ across all treatments) and NO$_3$-N
(average 0.8±0.6 kg ha$^{-1}$ across all treatments) fluxes above those of the control soils,
and while there were no significant differences between treatments between weeks 14
and 28, TN losses were higher from amended slurries between weeks 10 and 13
(Figure 2 – A1 and A2; Table S1). Similarly, application of unamended and amended
DSW did not increase TN and NO$_3$-N fluxes above those of the control soil and
treatments were not significantly different from each other (Figure 2 – C1 and C2, Table S1). These relatively low N leaching losses from dairy slurry were consistent with the relatively small amount (16.5%) of mineral N (mainly as NH$_4$-N) as a proportion of TN in the applied slurry (Table 2) and are consistent with the findings of Di et al. (1998), who measured dairy slurry leaching losses of 8 – 25 kg NO$_3$-N ha$^{-1}$ y$^{-1}$ in a lysimeter study comparing dairy slurry with inorganic fertilizer applications.

The mineralisation of the organic N load in the applied dairy slurries is influenced by variations in soil, weather, manure composition and management (van Es et al., 2006), and is quite a slow process, likely to extend beyond the experimental period of this study. It is likely, therefore, that repeated applications of dairy slurry over a longer timescale may result in higher amounts of leachate NO$_3$-N (Kayser et al., 2015) than were observed during the current study, although this may also have the added benefit of increasing the soil CEC and hence its ability to reduce NH$_4$ leaching losses without adversely impacting its hydraulic conductivity (Mishra et al., 2016).

Cumulative NH$_4$-N in leachate was highest for pig slurry amended with PAC and zeolite (1.97 kg ha$^{-1}$) and was tightly grouped with all other amended treatments and with unamended DSW (Figure 3 – C1). The cumulative amounts of NH$_4$-N leached from unamended pig and dairy slurries (1.25 and 1.19 kg ha$^{-1}$, respectively) were lower than those of DSW, but remained above those of the control soil (0.94 kg ha$^{-1}$). This further illustrates the ability of amended and unamended pig slurry, which had by far the highest NH$_4$-N concentration of the three applied slurries (Table 2), to nitrify in significant quantities, with consequent high levels of NO$_3$-N in leachate.

Ammonium-N leachate losses from dairy slurry are limited by the relatively low amounts of NH$_4$-N in the applied slurries (Table 2) and may also be affected by the
moderately high CEC (10.9 cmol kg\(^{-1}\)) of the soil. The higher NH\(_4\)-N losses from DSW were reflective of its high NH\(_4\)-N/TN ratio (73%) and its inability to nitrify to the same extent as pig slurry, which may have been affected by its relatively high C/N ratio (7.3).

A mass balance to estimate the relative cumulative amounts of slurry N leached (weeks 10 – 28) was carried out using:

\[
\text{% N leached} = \frac{(\Sigma \text{Mass } N_{\text{leachate}} - \Sigma \text{Mass } N_{\text{control soil}})}{\Sigma \text{Mass } N_{\text{applied slurry}}} \tag{2}
\]

where: \(\Sigma \text{Mass } N_{\text{leachate}}\) is the cumulative mass of TN measured in the leachate; \(\Sigma \text{Mass } N_{\text{control soil}}\) is the cumulative mass of TN leached from the control soil and \(\Sigma \text{Mass } N_{\text{applied slurry}}\) is the TN of the applied slurry, calculated by multiplying the applied slurry volume by its concentration. All of the TN in the DSW was leached for all treatments; however, the amount of TN in DSW was very low when compared with either pig or dairy slurries (Table 2). Approximately 70% of TN from unamended pig slurry and pig slurry amended with PAC and zeolite was leached, and this reduced to 45% for pig slurry amended with PAC. None of the TN in the dairy slurries (all treatments) was leached, and this was reflected in the insignificant differences in N leaching between the dairy slurries (unamended and amended) and the control soil between weeks 14 and 28 (Table S1). This finding supports the observation that the relatively low fraction of plant available N in dairy slurry combined with its high DM content (10%) and with the relatively high CEC of the soil reduces its overall potential for leaching and is consistent with the findings of Salazar et al. (2012), who, in a field experiment to compare the effects of dairy slurry application on N leaching losses with those from inorganic fertilizer, reported cumulative net N leaching losses < 1% of the applied slurry N, which comprised c. 65% organic N. The higher C/N
ratio of the dairy slurry (11.4±1.3) also indicates that it will have a slower
mineralisation process than either pig slurry (1.4±0.0) or DSW (7.3±0.2) (Table 2).

Total N and N$_{org}$ in leachate were dominated by their respective dissolved forms for
all slurries. Total dissolved N as a proportion of TN was highest for pig slurries (91%,
92% and 96% for unamended pig slurry, pig slurry amended with PAC and pig slurry
amended with PAC and zeolite, respectively) followed by DSW (90%, 96% and 96%
for unamended DSW, DSW amended with alum and DSW amended with alum and
zeolite, respectively). The average proportion of TN$_d$ to TN for dairy slurry (82%)
was closest to that of the control soil (72%), supporting the evidence that most of the
N leached from the dairy slurry columns was from the soil and not the applied slurry.
Dissolved organic N as a proportion of N$_{org}$ was highest for DSW (86%, 94% and
94% for unamended DSW, DSW amended with alum and DSW amended with alum
and zeolite, respectively), followed by pig slurries (84%, 89% and 93% for
unamended pig slurry, pig slurry amended with PAC and pig slurry amended with
PAC and zeolite, respectively). However, the average cumulative amount of DON
leached from pig slurries (86.3 kg ha$^{-1}$) was considerably higher than that from DSW
(54.3 kg ha$^{-1}$) and dairy slurries (21 kg ha$^{-1}$), highlighting its greater potential to
stimulate eutrophication processes and the proliferation of toxic phytoplankton in
aquatic ecosystems (Berman and Bronk, 2003). The average proportion of DON to
N$_{org}$ in leachate from unamended and amended dairy slurries (74%) was lower that
from either pig slurries or DSW, indicating that in the short term at least it may not be
as harmful to groundwater sources as the other more mobile slurries.

### 3.4 Leachate Carbon
The average cumulative TOC leached from unamended dairy slurry (82 kg ha\(^{-1}\)) was significantly higher than that from the control soil and from all other unamended and amended slurries which were not significantly different from each other, ranging from 48.2 to 35.6 kg ha\(^{-1}\) for PAC amended pig slurry and DSW amended with alum and zeolite, respectively (Figure 4, Table S2). This is reflective of the much higher TOC:TN ratios in dairy slurry compared to pig slurry and DSW (Table 2) which combined with a P deficiency, likely inhibited heterotrophic microorganism growth.

The average cumulative TOC loads for unamended and amended pig slurries were lower than those reported by O’Flynn et al. (2013), who measured leachate loads equivalent to c. 75 kg TOC and 240 kg TIC ha\(^{-1}\) in an eight month soil column experiment. Dairy slurry amended with PAC and with PAC and zeolite significantly reduced leachate TOC concentrations compared to unamended dairy slurry (Table S2). This was most likely due to the flocculation of the C-enriched dairy slurry particles at the soil surface by the PAC combined with small amounts of TOC adsorbed by the zeolite (Murnane et al., 2016). Total organic C fluxes were dominated by DOC, with average DOC/TOC ratios of 76% for control soil, 83% for unamended and amended dairy slurries, 75% for unamended and amended pig slurries, and 82% for unamended and amended DSW. The average amounts of TOC leached from unamended and amended slurries over the duration of the experiment, compared with the amounts applied (Eqn. 2), were negligible for both pig slurry and DSW (<1%), but were also very low for dairy slurry (average 2.5%). These low levels are consistent with the findings of Bolado-Rodríguez et al. (2010), who measured just 0.3 g TOC in leachate from air stripped pig slurry compared with 3.5 g applied in a soil column experiment.
The average cumulative TIC leached from all slurries and from the control soil was much higher than the corresponding TOC fluxes (Figure 4), with the highest load from unamended dairy slurry (142.3 kg ha\(^{-1}\)) and the lowest from pig slurry amended with PAC and zeolite (102.9 kg ha\(^{-1}\)). All unamended and amended slurry applications resulted in higher TIC leachate fluxes than the control soil except for pig slurry amended with PAC, pig slurry amended with PAC and zeolite, and dairy slurry amended with PAC; however, these differences were not significant (Table S2). There were significant reductions in leachate TIC from dairy slurry amended with PAC compared to unamended dairy slurry, likely due to flocculation by PAC of C enriched dairy slurry, but there were no significant differences between unamended and amended pig slurries and unamended and amended DSW (Table S2). Total inorganic C fluxes were dominated by DIC with average DIC/TIC ratios of 90% for control soil, 91% for unamended and amended dairy slurries, 92% for unamended and amended pig slurries, and 93% for unamended and amended DSW.

All of the applied TIC from the dairy slurries and DSW and an average 28% from the pig slurries, which had the highest concentration of TIC (Table 2), was leached (Eqn. 2) over the experimental duration, indicating the greater mobility of the mineralised C and its potential for leaching.

### 3.5 CO\(_2\) and CH\(_4\) emissions after land application

Emissions of CO\(_2\)-C from unamended pig slurry were highest on the day of slurry application (4.0±0.3 kg CO\(_2\)-C ha\(^{-1}\) h\(^{-1}\)) and reduced quickly between days 1 and 8, where they remained constant (average 1.0±0.3 kg CO\(_2\)-C ha\(^{-1}\) h\(^{-1}\)) until the end of the sampling period [Figure 5(A)]. This is reflective of the high TIC in leachate from pig
slurry, which can result in increased microbial activity and CO₂ emissions (Dumale et al., 2009; Cayuela et al., 2010). Slight, but insignificant increases in emissions from pig slurries were observed immediately after irrigation of the columns on days 5, 8 and 12 [Figure 5(A)], indicating that disturbance of surface applied slurries as well as change in soil moisture can result in increased CO₂ emissions (Miller et al., 2005; Huang et al., 2017). A similar pattern of increased, but lower, CO₂-C emissions than from pig slurries were observed for dairy slurries (1.2±0.2 kg CO₂-C ha⁻¹ h⁻¹) and DSW (1.1±0.1 kg CO₂-C ha⁻¹ h⁻¹) on the day of slurry application, followed by quick reductions between days 1 and 8 to averages of 0.3±0.0 and 0.6±0.1 kg CO₂-C ha⁻¹ h⁻¹, respectively (results not displayed).

Cumulative CO₂-C emissions averaged across the three treatments for each slurry type were highest for pig slurries (680±63 kg CO₂-C ha⁻¹), followed by DSW (515±59 kg CO₂-C ha⁻¹) and dairy slurries (486±215 kg CO₂-C ha⁻¹), and were all greater than those from the control soils (137±3 kg CO₂-C ha⁻¹) over the experimental duration [Figure 5(B)]. This is consistent with the findings of O’Flynn et al. (2013), who measured cumulative CO₂ emissions between c. 500 and 850 kg CO₂-C ha⁻¹ from unamended and PAC-amended pig slurries. The CO₂ emissions from dairy slurries were similar to those measured by Brennan et al. (2015) (450 kg CO₂-C ha⁻¹) in a laboratory-scale study to evaluate the impact of chemical amendments on GHG emissions. There were no statistical differences in cumulative CO₂ emissions between unamended and amended pig slurries or between unamended and amended DSW; however, dairy slurry amended with PAC and dairy slurry amended with PAC and zeolite, while not significantly different from each other, resulted in higher CO₂-C emissions than from unamended dairy slurry, which was not significantly different.
from the control soil (Table S3). This supports our earlier observation that C-enriched
dairy slurry particles may have flocculated on the soil surface when amended with
either PAC or PAC and zeolite, with the concomitant increase in CO₂ releases when
compared with unamended dairy slurry.

There were no CH₄ emissions from the control soil or applied slurries except from
unamended pig slurry, pig slurry amended with PAC, and pig slurry amended with
PAC and zeolite on day 1 (0.101±0.008, 0.084±0.009 and 0.106±0.011 kg CH₄-C ha⁻¹
h⁻¹, respectively) and day 2 (0.013±0.002, 0.007±0.004 and 0.014±0.001 kg CH₄-C
ha⁻¹ h⁻¹, respectively) (results not displayed). This response to treatment was also
noted by Sistani et al. (2010), who, in a field experiment to measure GHG emissions
from pig slurry by different application methods, reported elevated CH₄ fluxes
compared with the soil control for 3 to 5 d after application with very low or zero
emissions thereafter. In the current study, no CH₄ emissions were detected from either
untreated or treated pig slurries after day 2, as oxic conditions prevailed over the
preferred anoxic conditions required for CH₄ production, and there were no
significant differences between the treatments.

3.6 CO₂ and CH₄ emissions during storage

Emissions of CO₂ from stored raw undisturbed dairy and pig slurries, and DSW were
highest on day 1 (3.25±0.07, 9.90±0.12 and 3.72±0.08 kg CO₂-C ha⁻¹ h⁻¹, respectively)
and reduced rapidly between days 1 and 10 to averages of 0.99±0.26, 2.08±0.46 and
0.61±0.24 kg CO₂-C ha⁻¹ h⁻¹ between days 13 and 52 (results not displayed).
Cumulatively, raw pig slurry emitted the highest quantity of CO₂ (2,698±85 kg CO₂-C
ha$^{-1}$), followed by dairy slurry (1,179±53 kg CO$_2$-C ha$^{-1}$) and DSW (882±51 kg CO$_2$-C ha$^{-1}$) [Figure 6(A)].

Raw pig slurry had the highest cumulative CH$_4$ emissions (2,856±78 kg CH$_4$-C ha$^{-1}$), with much lower emissions from dairy slurry (40±32 kg CH$_4$-C ha$^{-1}$) and no emissions from DSW [Figure 6(A)]. The cumulative CO$_2$-C eq. emissions (comprising CO$_2$-C and CH$_4$-C) based on the predicted 100 yr. global warming potential (GWP$_{100}$) of 25 CO$_2$ eq. for 1 CH$_4$ (IPCC, 2007) were much higher from stored raw pig slurry (74,100±3,972 kg CO$_2$-C eq. ha$^{-1}$) than from either dairy slurry (2,177±1,693 kg CO$_2$-C eq. ha$^{-1}$) or DSW (882±512 kg CO$_2$-C eq. ha$^{-1}$) [Figure 6(B)]. The average CH$_4$ fluxes for pig and dairy slurries, respectively, were 338 and 9.2 mg m$^{-2}$ h$^{-1}$ and accounted for 46 and 96% of the total CO$_2$ eq. emissions. In an investigation into CO$_2$ and CH$_4$ emissions from pig manure storage facilities, Na et al. (2008) measured similar average CH$_4$ emissions of 306 mg m$^{-2}$ h$^{-1}$ with CH$_4$ contributing c. 95% of the total CO$_2$ eq. emissions. In a study to measure GHG emissions from stored dairy slurry on multiple farms, Le Richie et al. (2016) reported emissions ranging from 6.3 – 25.9 g CH$_4$ m$^{-2}$ d$^{-1}$ at average air temperatures of 18 °C and, similarly, Wood et al. (2014) measured emissions from stored dairy slurry of 5 – 15 g CH$_4$ m$^{-2}$ d$^{-1}$ for varying temperatures typically > 15 °C. These emissions are higher than those measured in the current study (average 0.22 g CH$_4$ m$^{-2}$ d$^{-1}$) and may reflect the reduced CH$_4$ production at low temperatures (10.9±0.7 °C in the current study) (Sommer et al., 2007), although this did not seem to impact the pig slurry as much. The high CO$_2$ eq. emissions from stored slurries, in particular pig slurry [Figure 6(B)], highlights the need to consider storage emissions when assessing GHG emissions from agricultural slurries (Rodhe et al., 2015).
3.7 Measurement of overall environmental impact of treatments

The overall impact of each treatment in terms of TN, TC, CO₂ and CH₄ is shown in Table 3. Of the treatments examined, unamended and chemically amended pig slurry had the highest cumulative CO₂ and CH₄ emissions and leaching losses of N and C. Although the dual amendment of zeolite and PAC/alum proved successful in reducing surface runoff losses of N, P and C (Murnane et al., 2016), they did not mitigate leaching losses and GHG emissions from soil columns and, moreover, actually increased contamination (gaseous and water) from the soil columns in the case of dairy slurry and DSW.

4 Conclusions

Of the three slurries examined, pig slurry has the greatest potential for N leaching to groundwater because of its high N concentrations, high proportion of mineral N, and ability to nitrify. The study found that N leaching from DSW is less likely than from pig slurry, given its typically lower N concentrations and higher C/N ratio. A single application of dairy cattle slurry represents the lowest N leaching risk, because of its typically high N₉₉₀ and low mineral N content; however, repeated applications are likely to result in increased soil mineral N with the possible risk of NO₃⁻-N in leachate, particularly in sandy soils.

In general, application of the amendments used in the current study did not significantly impact the N leaching potential from all applied slurries and while higher cumulative N losses were measured from amended compared to unamended dairy slurry, these are likely to be as a result of soil rather than slurry losses. Although there
were no leachate P losses, it is likely that removal of the macropore network in the
packed soil columns may have eliminated a major pathway for subsurface P transport
and it is possible that repeated slurry applications on natural undisturbed soil may
eventually result in P leaching to groundwater, although this is more likely for organic
soils and less likely for sandy soils.

Application of amendments to slurries had no impact on C leaching or on CO$_2$ and
CH$_4$ emissions except for dairy slurries, where PAC only and PAC and zeolite-
amended dairy slurries reduced the amounts of TOC and TIC leached, but increased
CO$_2$ emissions compared to unamended dairy slurry.

The column experiment used in this study represented a worst case scenario of winter
slurry application (on bare soil with no crop growth) followed by persistent rainfall.
Even though single application of unamended and amended slurries were investigated,
the results indicate that the resultant environmental impacts in terms of N and C
leaching and cumulative CO$_2$ and CH$_4$ emissions may be adversely affected by
amended dairy slurries, primarily due to increased CO$_2$ emissions. This is also true of
DSW but to a much lesser extent, while the amendments applied to pig slurries had no
effect. While zeolite and PAC amendments were previously shown to be effective in
mitigating surface runoff losses of N, P and C, particularly from dairy slurry, these
benefits may be offset by their deleterious impact on leaching and CO$_2$ emissions. The
combined N and C leaching and gaseous losses were highest for pig slurry, and this
would seem to pose the greatest short term environmental threat of the three slurries
examined.
This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.
References


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Salazar, F., Martínez-Lagos, J., Alfaro, M., Misselbrook, T., 2012. Low nitrogen leaching losses following a high rate of dairy slurry and urea application to pasture


Table 1 Characteristics of the soil used in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk density</td>
<td>1.06±0.13</td>
<td>g cm$^{-3}$</td>
</tr>
<tr>
<td>% sand</td>
<td>46.9±2.1</td>
<td>%</td>
</tr>
<tr>
<td>% silt</td>
<td>36.5±1.2</td>
<td>%</td>
</tr>
<tr>
<td>% clay</td>
<td>16.1±0.8</td>
<td>%</td>
</tr>
<tr>
<td>D$_{10}$</td>
<td>0.05±0.00</td>
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</tr>
<tr>
<td>D$_{60}$</td>
<td>0.10±0.01</td>
<td>mm</td>
</tr>
<tr>
<td>Coefficient of uniformity</td>
<td>1.95±0.22</td>
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</tr>
<tr>
<td>Organic matter content</td>
<td>5.19±0.28</td>
<td>%</td>
</tr>
<tr>
<td>Total C</td>
<td>2.38±0.01</td>
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</tr>
<tr>
<td>Total N</td>
<td>0.28±0.01</td>
<td>%</td>
</tr>
<tr>
<td>C:N</td>
<td>8.65±0.25</td>
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<tr>
<td>pH</td>
<td>5.99±0.20</td>
<td></td>
</tr>
<tr>
<td>Soil extractable P</td>
<td>88.5±7.8</td>
<td>mg kg$^{-1}$</td>
</tr>
<tr>
<td>Soil extractable K</td>
<td>10.6±11.3</td>
<td>mg kg$^{-1}$</td>
</tr>
<tr>
<td>Soil extractable Ca</td>
<td>1,392±105</td>
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<tr>
<td>Soil extractable Mg</td>
<td>118.5±7.8</td>
<td>mg kg$^{-1}$</td>
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<tr>
<td>Soil extractable Al</td>
<td>631±77</td>
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<tr>
<td>Cation exchange capacity</td>
<td>10.90±0.82</td>
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<tr>
<td>Water soluble organic C</td>
<td>58.5±11.4</td>
<td>mg kg$^{-1}$</td>
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<tr>
<td>Soil water extractable P</td>
<td>1.10±0.49</td>
<td>mg kg$^{-1}$</td>
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Table 2: Slurry characterizations (mean ± standard deviation) \((n=3)\) for total N (TN), ammonium-N \((\text{NH}_4\text{-N})\), total P (TP), dissolved reactive P (DRP), total organic C (TOC), total inorganic C (TIC), pH and dry matter (DM).

<table>
<thead>
<tr>
<th>Slurry type</th>
<th>TN</th>
<th>NH(_4)-N</th>
<th>TP</th>
<th>DRP</th>
<th>TOC</th>
<th>TIC</th>
<th>pH</th>
<th>DM</th>
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<tbody>
<tr>
<td>Dairy slurry</td>
<td>1,158±24</td>
<td>192±6</td>
<td>540±2</td>
<td>344±3</td>
<td>13,120±1,250</td>
<td>46±9</td>
<td>6.75±0.06</td>
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<td>Pig slurry</td>
<td>3,689±119</td>
<td>3,364±15</td>
<td>199±3</td>
<td>137±1</td>
<td>4,900±130</td>
<td>236±105</td>
<td>7.95±0.07</td>
<td>2.21±0.11</td>
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<tr>
<td>Dairy soiled water</td>
<td>105±2</td>
<td>76.8±0.6</td>
<td>15.4±0.2</td>
<td>14.1±0.1</td>
<td>602±7</td>
<td>169±2</td>
<td>7.14±0.07</td>
<td>0.28±0.01</td>
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</table>
**Table 3** Measurement of overall environmental impact of treatments in terms of cumulative total N (TN), total C [total organic C (TOC) and total inorganic C (TIC)] losses (kg ha\(^{-1}\)) and cumulative carbon dioxide (CO\(_2\)) and methane (CH\(_4\)) emissions (expressed as kg CO\(_2\)-C eq. ha\(^{-1}\)). (1 CH\(_4\) = 25 CO\(_2\) eq.)

<table>
<thead>
<tr>
<th>Slurry type</th>
<th>Treatment</th>
<th>TN</th>
<th>TOC</th>
<th>TIC</th>
<th>CO(_2) + CH(_4)</th>
<th>Total</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>kg ha(^{-1})</td>
<td></td>
<td>kg ha(^{-1})</td>
<td>(kg CO(_2)-C eq. ha(^{-1}))</td>
<td></td>
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<tr>
<td><strong>Dairy</strong></td>
<td>Unamended</td>
<td>25</td>
<td>82</td>
<td>142</td>
<td>251</td>
<td>500</td>
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<tr>
<td></td>
<td>+PAC</td>
<td>60</td>
<td>38</td>
<td>104</td>
<td>671</td>
<td>873</td>
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<tr>
<td></td>
<td>+PAC and zeolite</td>
<td>43</td>
<td>43</td>
<td>119</td>
<td>536</td>
<td>741</td>
</tr>
<tr>
<td><strong>Pig</strong></td>
<td>Unamended</td>
<td>181</td>
<td>42</td>
<td>117</td>
<td>740</td>
<td>1,081</td>
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<tr>
<td></td>
<td>+PAC</td>
<td>137</td>
<td>48</td>
<td>106</td>
<td>737</td>
<td>1,028</td>
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<tr>
<td></td>
<td>+PAC and zeolite</td>
<td>180</td>
<td>40</td>
<td>103</td>
<td>633</td>
<td>956</td>
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<tr>
<td><strong>DSW</strong></td>
<td>Unamended</td>
<td>82</td>
<td>38</td>
<td>134</td>
<td>447</td>
<td>701</td>
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<tr>
<td></td>
<td>+alum</td>
<td>91</td>
<td>37</td>
<td>123</td>
<td>556</td>
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<td></td>
<td>+alum and zeolite</td>
<td>89</td>
<td>36</td>
<td>115</td>
<td>543</td>
<td>782</td>
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Figure 1 Schematic diagrams of (A) typical column setup for leachate sampling and (B) column setup during gas sampling (Not to scale)
Figure 2 Average (n=3) weekly fluxes of total N (TN) and nitrate-N (NO$_3$-N) for dairy slurry (A1–A2), pig slurry (B1–B2) and dairy soiled water (DSW) (C1–C2). Error bars indicate SD.
Figure 3 Average cumulative fluxes of total N (TN), nitrate-N (NO$_3$-N) and ammonium-N (NH$_4$-N) for control soil and all unamended and amended slurries (A1, B1 and C1). Error bars indicate SD.
Figure 4 Average (n=3) cumulative fluxes of total organic C (A1) and total inorganic C (B1) for control soil and all unamended and amended slurries. Error bars indicate SD.
Figure 5 Average CO₂ emissions from control soil and from soil which was surface applied with unamended and amended pig slurries and irrigated on days 5, 8 and 12 (R5, R8 and R12) (A); average cumulative CO₂ emissions from control soil and from soil which was surface applied with unamended and amended slurries (B). Error bars indicate SD, n=3
Figure 6 Average cumulative CO$_2$ and CH$_4$ emissions from stored undisturbed raw dairy and pig slurries and DSW (A); average cumulative total equivalent CO$_2$ emissions (comprising CO$_2$ and CH$_4$) from stored undisturbed raw dairy and pig slurries and DSW (1 CH$_4$ = 25 CO$_2$ eq.) (B). Error bars indicate SD, n=3.