Incidental phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry.

Title	Incidental phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry.
Author(s)	Brennan, Raymond B.;Healy, Mark G.
Publication Date	2012-09
Publisher	Elsevier
Repository DOI	http://dx.doi.org/10.1016/j.scitotenv.2012.09.078

Published as: Brennan, R.B., Healy, M.G., Grant, J., Ibrahim, T.G., Fenton, O. 2012. Incidental phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry. Science of the Total Environment 441: 132 – 140.

http://dx.doi.org/10.1016/j.scitotenv.2012.09.078

Incidental phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry

R.B. Brennan[1, 2, 3*], M.G. Healy[1], J. Grant[4], T.G. Ibrahim[2], O. Fenton[2]

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

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

[3]Dept. Crop, Soil, and Environmental Sciences, Division of Agriculture, University of Arkansas, Fayetteville, AR, USA.

[4]Teagasc, Ashtown, Dublin 15, Rep. of Ireland

*Corresponding author: Tel: +1479 575 5720 E-mail address: rbrennan@uark.edu; raymond21brennan@gmail.com

Abstract

Chemical amendment of dairy cattle slurry has been shown to effectively reduce incidental phosphorus (P) losses in runoff; however, the effects of amendments on incidental nitrogen (N) losses are not as well documented. This study examined P and N losses in runoff during three simulated rainfall events 2, 10 and 28 days after a single application of unamended/chemically amended dairy cattle slurry. Twenty-five hydraulically isolated plots, each measuring 0.9 m by 0.4 m and instrumented with runoff collection channels, were randomly assigned the following treatments: (i) grass-only, (ii) slurry-only (the study-control), (iii) slurry amended with industrial grade liquid alum comprising 8% Al_2O_3, (iv) slurry amended with industrial grade liquid poly-aluminum chloride (PAC) comprising 10% Al_2O_3, and (v) slurry amended with lime. During the first rainfall event, lime was ineffective but alum and PAC effectively reduced dissolved reactive P (DRP) (by 95 and 98%, respectively) and total P (TP) flow-weighted-mean-concentrations (by 82 and 93%, respectively) in runoff compared to the study-control. However, flow-weighted-mean-concentrations of ammonium-N (NH_4-N) in runoff were increased with alum- (81%) and lime-treated (11%) slurry compared to the study-control whereas PAC reduced the NH_4-N by 82%. Amendments were not observed to have a significant effect on NO_3-N losses during this study. Slurry amendments reduced P losses for the duration of the study, whereas the effect of amendments on N losses was not significant following the first event. Antecedent volumetric water content of the soil or slope of the plots did not appear to affect runoff volume. However, runoff volumes (and consequently loads of P and N) were observed to increase for the chemically amended plots compared to the control and soil-only plots. This work highlights the importance of considering both P and N losses when implementing a specific nutrient mitigation measure.

Keywords: alum; poly-aluminum chloride; lime; runoff; amendments; management

1. Introduction

Incidental losses of phosphorus (P) and nitrogen (N) occur when rainfall interacts directly with inorganic and organic fertilizers spread on the land surface (Preedy et al., 2001; Smith et al., 2001a; Withers et al., 2003; Buda et al., 2009). Incidental P and N losses are dependent on factors such as: the amount and type of fertilizer or manure applied (Kleinman and Sharpley, 2003), timing of the rainfall event after application of fertilizer or manure (Pote et al., 2001; Smith et al., 2007; Allen and Mallarino, 2008; Hanrahan et al., 2009), the volume of runoff generated, antecedent hydrologic conditions and field position, flow path length (McDowell and Sharpley, 2002), vegetative cover (Zhang et al., 2003) and surface slope (Alaoui et al., 2011). Incidental P losses in runoff following land application of dairy cattle slurry are dominated by particulate P (PP) (Withers and Bailey, 2003) and N losses by ammonium-N (NH_4-N) (Smith et al., 2001a). While P is generally considered the limiting nutrient in freshwater systems (Correll, 1998; Hudnell, 2010; Paerl, 2008; Shindler et al., 2008), N losses also pose a significant risk to water quality (Johnes et al., 2007; Vitousek et al., 2009).

Chemical amendment of dairy cattle slurry (Elliot et al., 2005; Torbert et al., 2005; Brennan et al., 2011a, b) and poultry litter (Moore and Edwards, 2007) has been effective at reducing P losses in surface runoff following land application. As a result, manure amendment is a recommended best management practice (BMP) in the USA, and federal support is available to aid its implementation (Sharpley et al., 2006; SERA-17, 2012; USDA-NRCS, 2012). There have been a large number of laboratory-scale studies that have examined the effect of amendments on P solubility in dairy and swine slurry (Dao, 1999; Dao and Daniel, 2002; Dou and Cavigelli, 2003; Torbert et al., 2005). Torbert et al. (2005) amended composted dairy manure with ferrous sulphate, gypsum and lime (each at 3:1 metal-to-total phosphorus (TP) ratio) before surface application and immediately prior to a 40-min overland event equivalent to a rainfall intensity of 12.4 cm h^{-1}. Ferrous sulphate reduced dissolved reactive phosphorus (DRP) loss by 66.3%, while gypsum and lime amendments increased DRP loss. In a plot study, Smith et al. (2001b) amended swine manure with alum and aluminum chloride ($AlCl_3$) at two stoichiometric ratios (0.5:1 and 1:1 Al: TP). Dissolved reactive phosphorus reductions for alum and $AlCl_3$ at the lower ratio were 33% and 45%, respectively, and 84% for both amendments at the higher ratio.

While the effectiveness of amendments is well established, there is less information on the effect of amendments on N loss to runoff and runoff properties. It is known that land application of dairy cattle slurry on grassland (Nunez et al., 2001) and arable land increases runoff volumes which affects N and P losses (Smith et al., 2007). In addition chemical amendment of dairy cattle slurry affects the texture and rate of drying of slurry following land application (Brennan et al., unpublished data) which may impact runoff volumes. Approximately 50% of the N in dairy cattle slurry is in an inorganic form (NH_4-N from urea in the urine component of slurry) and although this is plant available, as much as 80% of it is lost through volatilization in a short time period after slurry application. Chemical amendments have been shown to significantly reduce ammonia (NH_3) volatilization following land spreading of dairy cattle slurry (Lefcourt and Meisinger, 2001). This is likely to increase the NH_4-N available for uptake by plants and potentially runoff.

Chemical amendments reduce P solubility in poultry, swine and dairy cattle manure. However, slurry N is much more mobile than P and its loss pathways are more complex. Therefore, amendments which change the properties of slurry may influence N transformations following land application, and may result in increased N losses to the atmosphere or in surface runoff. This is sometimes referred to as ‘polluting swapping’ (Stevens and Quinton, 2009).Therefore, any study investigating the efficacy of any potential P mitigation measure, such as those described above, must also consider the ‘pollution swapping’ that may arise from their use. To the authors’ knowledge, this is the first study to examine the impact of chemical amendment of dairy cattle slurry on incidental losses of both N and P in runoff.

The specific objectives of this study were to investigate (i) incidental N and P losses from soil-only, slurry-only and amended slurry treatments (ii) the effect of chemical amendment of dairy cattle slurry on runoff volume, volumetric water content, and time to runoff, and (iii) the short-term effect of land application of chemically amended dairy cattle slurry on soil chemical properties.

2. Materials and Methods

2.1. Study site characterization

The site work was carried out between 11th September 2010 and 18th October 2010, on a 0.6-ha isolated plot on a beef farm located at Teagasc, Johnstown Castle, Environmental Research Centre (latitude 52º 17’N, longitude 6º 29’W), in the southeast of Ireland. This area has a cool maritime climate, a mean annual precipitation of 1002 mm (effective rainfall (rainfall - evapotranspiration) from between 400 to 500 mm), and a mean annual temperature of 10°C (Ryan and Fanning, 1996).

The location of 25 isolated plots within the 0.6 ha site was determined by: topography/slope, soil texture/drainage assessment, depth to watertable, and soil nutrient analysis. Within the 25 plots (0.9 m by 0.4 m), treatments were randomly assigned in five blocks (Fig 1). The site had undulating topography with a 6.7% slope along the length of the site and an average slope of 3.6% across the site. For textural analysis (pipette method, B.S.1377-2:1990 (BSI, 1990)), 10 cm-deep soil samples (n=3) were taken from a 1-m^2 area at the top, middle and bottom of the 0.6 ha plot (Fig 1). Electromagnetic conductivity (characterization to 4 m below ground level (bgl)) and resistivity of the 0.6-ha site were used to infer overall textural and drainage characteristics. The top of the plot comprised gravelly clay with pockets of silty/clayey gravel underlain by silt/gravel (20 to 26 mS m^{-1}), and was relatively well-drained compared to the lower part of the site, which comprised silt/clay and was poorly drained (>26 mS m^{-1}). The median perched watertable depth in three piezometers (top, middle and bottom of slope) was 0.6 m bgl on site. The nutrient status of the soil at these locations (P, potassium (K), and magnesium (Mg)), determined using Morgan’s extractant (Morgan, 1941), are presented in Table 1. Soil pH (n=3) was determined using a pH probe and a 2:1 ratio of deionised water to soil (Table 1). Each plot was installed, isolated and instrumented with a runoff collection channel (Fig 1). A composite soil sample (100 mm) was taken from each plot (before (t_0) and after the experiment (t_{30})) and soil pH, Morgan’s P, K, Mg and lime requirement (LR) were determined. In addition, composite soil samples (25 mm) were taken from each plot at t_0 and t_{30} for water extractable P (WEP) determination.

2.2. Slurry analysis

Dairy cattle slurry was collected from the dairy farm at the Teagasc, Environmental Research Centre, Johnstown Castle, in September of 2010. The storage tanks were agitated and slurry samples were transported to the laboratory in 25-L drums. Slurry samples were stored at 4°C prior to land application. Slurry pH was determined using a pH probe (WTW, Germany). The TP of the dairy cattle slurry was determined after Byrne (1979). Total potassium (TK), total nitrogen (TN) and TP were carried out colorimetrically using an automatic flow-through unit (Varian Spectra 400 Atomic Absorption instrument). The WEP of slurry and amended slurry was measured at the time of land application (1:100 dry matter slurry: deionised H_2O) after Kleinman et al. (2007), and NH_4-N of slurry and amended slurry was extracted by shaking 50 g of slurry in 1 L of 0.1 M hydrochloric acid (HCl) on a peripheral shaker for 1 hr and filtering through No. 2 Whatman filter paper at the time of application. The results of the slurry analysis are shown in Table 2. The slurry used in this study was typical of slurry found on farms in Ireland (Fenton et al., 2011). The slurry TN, TP, NH_4-N and TK were constant across samples. The WEP of slurry was decreased significantly by all alum and PAC amendments. Alum addition reduced the slurry pH from approximately 7.1 to 6.5, while lime addition increased the slurry pH to 8.8.

2.3. Treatments

The five treatments examined in this study were (i) grassed soil-only (referred to as soil-only hereafter) (ii) slurry applied to grassed soil (the study-control) (iii) slurry amended with industrial grade liquid alum ($Al_2(SO_4)_3.nH_2O$), comprising 8% Al_2O_3 (iv) slurry amended with industrial grade liquid PAC ($Aln(OH)mCl_3n\text{-}m$), comprising 10%Al_2O_3,and(v) slurry amended with lime ($Ca(OH)_2$). The slurry and amendments were mixed by shaking in 2-L containers for 30 s immediately prior to land application. In practice, it is likely that amendments would be mixed with the slurry in storage tanks during slurry agitation, which normally occurs within 24 h of land application. Two days before the first rainfall simulation, slurry and amended slurry were applied directly to the surface of the grassed soil. Slurry application rates were equivalent to 33 m^3 slurry ha^{-1}(42 kg TP ha^{-1}), the rate most commonly used in Ireland (Coulter and Lalor, 2008). Amendments were applied at stoichiometric ratios determined based on results of Brennan et al. (2011b). Alum was applied at a rate of 1:1 (Al: TP); PAC at a rate of 0.85:1 (Al: TP); and lime at a rate of 3.9:1 (Ca:TP). Land application of treatments was staggered over three days and applied in blocks to allow for the first rainfall event (RS1) two days after land application of slurry.

2.4. Rainfall event simulation and plot design

Two identical portable multi-drop ‘Amsterdam type’ rainfall simulators, described by Bowyer-Bower and Burt (1989), were used in this study. These rainfall simulators have been used on similar permanent grassland sites and soil types (Kurz et al., 2006; Kramers et al., 2009; O’Rourke et al., 2010). The rainfall simulators were designed to distribute rainfall over a surface area of 0.5 m^2 and were calibrated to deliver rainfall at an intensity of 11 mm hr^{-1}. The rainfall simulator water had average concentrations for the three rainfall simulation events of 0.05 mg NH_4-N L^{-1}, 4.61 mg nitrate-N (NO_3-N) L^{-1}, 0.002 mg DRP L^{-1} and 0.004 mg TP L^{-1}.

In order to ensure the absence of edge effects, the rainfall simulators were located directly above study plots – each measuring 0.36 m^2 in area. The plots were isolated using 2.2 m-long, 100 mmdeep rigid plastic sheets, which were pushed 50 mm into the soil to isolate three sides of the plot. The runoff collection channel was placed at the bottom of the slope (Fig 1). Plots were orientated with longest dimension in the direction of the slope (average 3.6%). The runoff collector comprised a polypropylene plastic U-shaped channel piece, which was cut in half and wedged against the soil at a depth of approximately 25 mm below the soil surface (Fig 1). A 400 mm-wide edging tool was used to cut the soil to ensure a good seal between soil and collector. The plots were left uncovered for two weeks prior to first rainfall simulation to allow natural rainfall to wash away soil disturbed by inserting the isolators. Natural rainfall was excluded from the plots between time of slurry application and RS1. Thereafter, plots were exposed to natural rainfall. Natural rainfall, together with the average simulated rainfall applied for each of the rainfall simulations, is shown in Fig 2. The grass on all plots was clipped to a height of 50 mm two days prior to application of treatments to simulate the spreading of slurry following silage cutting, which is common practice in Ireland. The second rainfall event (RS2) was 10 days after the original application (t = 12 d) and the third (RS3) after 28 days (t = 30 d).

Soil Moisture deficit (SMD) for the entire landscape position was estimated using the grassland Hybrid model of Schulte et al. (2005). For all events, rainfall simulator amounts (mm) were added to actual daily rainfall data and the SMD for each subsequent day was estimated (based on well, moderately and poorly drained soil). When SMD values returned to values achieved using actual rainfall data, the subsequent simulated rainfall event took place. The volumetric water content of soil in each plot was measured immediately prior to each rainfall simulation event using time domain reflectrometry (Delta-T Devices Ltd., Cambridge, UK), which was calibrated to measure resistivity in the upper 50 mm of the soil in each plot.

2.5 Runoff sample collection and analysis

Surface runoff was judged to occur once 50 ml of water was collected from the runoff collection channel and the time from start of rainfall simulation to runoff of 50 ml being the time to runoff (TR). Samples were collected every 5 min for RS1, and every 10 min for RS2 and RS3. Surface runoff was collected for 30 min once runoff commenced until the rainfall simulator was switched off to allow the flow-weighted mean concentration (FWMC) to be calculated (Kurz et al., 2006). For the third rainfall event, water was sprayed gently on the plots using a watering can until surface ponding occurred in order to complete rainfall simulations in daylight hours.

Immediately after collection, runoff water samples were filtered through 0.45μm filter paper and a subsample was analyzed colorimetrically for DRP, NO_3-N, NO_2-N and NH_4-N using a nutrient analyzer (Konelab 20, Thermo Clinical Labsystems, Finland). A second filtered subsample was analyzed for total dissolved phosphorus (TDP) using acid persulphate digestion. Unfiltered runoff water samples were analyzed for TP with an acid persulphate digestion. Particulate phosphorus was calculated by subtracting TDP from TP. The DRP was subtracted from the TDP to give the dissolved un-reactive phosphorus (DUP). All samples were tested in accordance with the Standard Methods (APHA, 2005).

2.6 Data analysis

Runoff ratio (RR) for each plot and for the duration of each simulated rainfall event was calculated by dividing the amount of water generated in overland flow by the amount of rainfall applied. As the plots were the same size, there was no scale effect (Wainwright and Parsons, 2002; Norbiato et al., 2009). Differences in RR between plots result from differences in soil permeability (Norbiato et al., 2009) (runoff ratio increases with a decrease in permeability), slope (Alaoui et al., 2011) (increasing slope will increase RR) and depth of unsaturated zone. A higher RR results from wetter rainfall pre-events and/or rainfall event conditions.

The structure of the data set was a blocked one-way classification (treatments) with repeated measures over time (rainfall events (RS1-RS3)). The analysis was conducted using Proc Mixed in SAS software (SAS, 2004) with the inclusion of a covariance model to estimate the correlation between rainfall events. A large number of covariates were recorded, including measurements on the simulators and for each analysis; this set of covariates was screened for any effects that should be included in an analysis of covariance. The interpretation was conducted as a treatment by time factorial. Comparisons between means were made with compensation for multiple testing effects using the Tukey adjustment to p-values. Significant interactions were interpreted using simple effects before making mean comparisons. In order to ensure that variation did not affect the experiment, STP was included as a variable in the statistical analysis. Slurry concentration, which was of much greater significance in terms of P concentrations in runoff following slurry application, was uniform within each block.

3. Results

3.1 Incidental nutrient losses over three rainfall events

The FWMC and total loads of DRP and TP for all treatments over the three rainfall simulation events are presented in Fig 3. Slurry application increased the FWMC and total loads of DRP and TP. Alum and PAC were equally effective at reducing FWMCs of DRP and TP compared to the study-control. Lime amendment resulted in increased FWMCs of DRP and TP compared to the study-control, with total loads for the lime treatment approximately 2 times greater than for slurry DRP and TP. When total loads were considered, PAC performed better than alum in reducing total loads of DRP. The effects of amendments on P loss were not significant for RS2 and RS3, which is likely a result of available P being leached from the soil.

The FWMC and total loads of NH_4-N and NO_3-N for all treatments are presented in Fig 4. The addition of alum resulted in an increase in the FWMC of NH_4-N compared with the study-control, while both lime and PAC treatments decreased the NH_4-N loss. In contrast, all amendments resulted in an increase in the FWMC of NO_3-N compared with the study-control. The PAC amendment was the only amendment which decreased total loads of NH_4-N to below those of the study-control. In contrast, both alum and lime amendments resulted in an increase in NH_4-N loads compared with the slurry treatment. Nitrite losses were negligible and were equivalent to approximately 1.9% of NO_3 for all samples and, for this reason, were not plotted in Fig 4.

3.2 Runoff characteristics

The time from start of rainfall simulation event to commencement of runoff event is shown in Fig 5. Time to runoff was generally longer for RS2 and shorter for RS3 (pre-wetted plots). No clear patterns were observed between treatments and differences were not significant. Total runoff volumes for the study were similar for soil and alum treatments (3990 ml 3930 ml), lower for the slurry treatment (3670 ml) and higher for lime and PAC treatments (4780 ml and 4460 ml). The differences observed between treatments were not statistically significant. There was no experimental effect on TR across all treatments when rainfall and rainfall intensity were included as covariates in the model. Both covariates showed a quadratic effect. Although there were no treatment effects observed for volumetric water content (VMC), RR and volume runoff, significant event effects were observed. Antecedent SMD conditions before all rainfall simulations for different drainage classes are presented in Fig 2. Soil moisture deficit was similar for all three rainfall events.

3.3 Soil test P, K, LR and pH

Soil test P, WEP, Mg, K, pH and LR results from analysis of plots before (t_0) and at the end of the experiment (t_{30}) are presented in Table 3. Average STP, Mg and K concentrations before the start of the experiment were similar for soil (5.5, 182 and 58 mg L^{-1}), slurry (4.5, 173 and 57 mg L^{-1}) and amended plots (from 4.3 to 5.9 mg L^{-1}, from 160 to 194 mg L^{-1} and from 53 to 59 mg L^{-1}). At the end of the experiment, STP increased by 13% in soil-only plots and by 28 to 34% in slurry, PAC and alum. Lime showed an 8.8% decrease in STP. At the end of the experiment, soil K increased for all treatments. Soil WEP decreased between t_0 and $t_{30}$for soil-only, alum-amended and PAC plots (20, 4 and 37%) and increased for study-control and lime-amended plots (42 and 64%).

4. Discussion

Under the European Union (EU) Water Framework Directive (WFD) (EU WFD; 2000/60/EC, OJEC, 2000), the water quality of surface and ground waters should be of ‘good status’ by 2015. Small amounts of P losses may contaminate large quantities of water and, therefore, incidental losses are of concern, in particular, for flashy events during baseflow conditions. Chemical amendment of dairy slurry has been shown to be effective in this regard. Moving from laboratory to field scales allows incidental losses to be simulated using *in-situ* soil and drainage conditions. The impact of slurry and amended slurry on soil pH, infiltration and runoff volumes, concentrations and loads, are all important when assessing the feasibility of a particular amendment.

4.1 Incidental losses for all rainfall events

In order to assess the adverse effects of discharge of incidental losses to a surface waterbody, it is critical to examine both runoff nutrient concentrations and total loads. Statistical analysis showed that differences in runoff volume between treatments were not significant. The addition of lime to soil or slurry, which is applied directly to soil, can change soil hydraulic characteristics such as infiltration, water retention and hydraulic conductivity, and may lead to lower (Roth and Pavan, 1991) or higher (Tarchitzky et al., 1993) runoff volumes. The increase in P loss as a result of lime amendment may be also due to an increase in the pH of the lime-amended slurry. Penn et al. (2011) found that in order for calcium (Ca)-phosphate bonds to remain stable, the pH must remain in a range of 6.5 to 7.5. In the present study, the average pH of the soil on the study site was 6.0 and the pH of the lime-amended slurry was 8.8 at the time of application. Brennan et al. (2011a) showed that the pH of lime-amended dairy cattle slurry increased in the first 24 hr following land application. The slurry pH was too high for Ca-P bonds to be stable during RS1 and when the slurry and soil interacted and reached equilibrium, the soil pH was lower than the optimal pH for the formation of Ca-P bonds. This may explain why reductions were not observed during RS2 and RS3. In the Brennan et al. (2011b) study, lime was applied at 10:1 Ca:TP compared to 3.9:1 in the present study, and this is possibly the reason for the difference in performance. In addition, the soil used in the Brennan et al. (2011b) study had a pH of 7.45 compared to 5.94 in the present study.

The reductions achieved in this study are consistent with the findings in Brennan et al. (2011b) with alum being the most effective amendment at reducing incidental PP and TP losses, while PAC was most effective at reducing DRP losses. Incidental P losses accounted for the majority of P losses from the study-control plots, with approximately 75% of DRP, 72% of DUP, 94% of PP and 83% of TP losses, measured over the three rainfall events, occurring during RS1. While incidental losses were significantly reduced in the alum and PAC-amended plots, the effect of amendments on chronic loss of P from the plots was not clear, as differences in runoff concentrations during RS2 and RS3 were not statistically different to the study-control. Studies have shown that chemical amendments can reduce incidental and chronic P losses (long-term P losses to runoff arising from elevated STP (Buda et al., 2009)) from soils receiving amended poultry litter (Moore and Edwards, 2005 and 2007). Amendments must be an ongoing practice for every manure application to effectively reduce P losses. Ultimately, P application must be balanced with crop P requirements to avoid chronic P loss.

In the present study, chemical amendment of dairy cattle slurry had no significant effect on NO_3-N concentration or load in runoff water. Alum increased the FWMC and load of NH_4-N compared to the study-control during the first rainfall event, PAC reduced the FWMC and load of NH_4-N and lime had no effect on the FWMC but increased the load of NH_4-N due to an increase in runoff volume. Dairy cattle slurry is high in NH_4-N which explains the high NH_4-N in runoff during RS1 (Smith et al., 2007). In a gas chamber experiment, Brennan et al. (unpublished data), using the same amendments as Brennan et al. (2011b), found that alum and PAC reduced NH_3 emissions from land applied slurry by up to 93% while lime amendment resulted in a two-fold increase in NH_3 emissions. The increase in NH_4-N load observed for the alum treatment during RS1 was likely caused by a decrease in NH_3 volatilization, which resulted in more NH_4-N remaining on the soil surface and being available for uptake by runoff. The difference between alum and PAC treatments indicates that PAC maybe more effective at binding NH_4-N which has not been volatilized on the soil surface, thereby reducing loss to runoff. The reduction in NH_4-N concentrations in runoff between RS1 and RS2 across all treatments, including the study-control, was likely due to nitrification occurring in the soil following slurry application and interaction with the soil. Smith et al. (2007) added dairy cattle slurry at a rate 75 m^3 ha^{-1} to grassed plots and reported soluble N (NH_4-N+NO_3-N) concentrations ranging from 2 mg L^{-1} to 14 mg L^{-1}, which was comparable to the average FWMC of soluble N observed in the present study (6.3 mg L^{-1}). The results of the present study results suggest that PAC is the most suitable amendment, as there was no increase in N losses compared to the study-control. This study did not examine the effect of amendments on N leaching losses. This work highlights the need to examine the pollution swapping effects of all P mitigation practices.

4.2 Runoff characteristics

In the current study, differences in slope of plots were not shown to be significant. All plots had the same landscape position mid-way between a down-gradient river and an up-gradient groundwater divide. Other studies have shown greater differences in slope at different landscape positions. Kleinman et al. (2006) investigated P and N losses in runoff from 1 x 2 m plots under simulated rainfall conditions during wet and dry periods in two landscape positions, foot slope (6%) and mid-slope (30%). Kleinman et al. (2006) showed that antecedent soil moisture at the foot-slope during the spring resulted in quicker runoff generation times and greater volumes of runoff.

In a homogeneous soil, runoff ratios should increase with VWC. The fact that this relationship was not always found in the current study for soil-only plots may be due to local heterogeneity. After slurry application, this relationship was more evident, which infers that mixing of soil and slurry leads to greater spatial homogeneity of water distribution and saturation. For amended slurry, the higher variability between VWC and runoff ratio (often a variable relationship) suggests that the amendments had a sealing effect. Within the timeframe of this study, it was not possible to assess the long-term effect of amendments on soil physical characteristics. As time from slurry application increases, soil conditions will return to a more heterogeneous state, whilst amendments may delay this process.

4.3 STP, K, LR and pH

In the present study, observed differences in soil nutrient concentrations following chemical amendment were not statistically significant. There were, however, noticeable changes in soil pH for some plots. These changes identify a need to examine the effect of chemical amendments on long-term P dynamics in soil following application of chemically amended dairy cattle slurry. Studies to date involving chemical amendment of dairy slurry have largely focused on reducing P solubility in dairy cattle slurry (Dao and Daniel, 2002; Dou et al, 2003; Brennan et al., 2011a) and mitigating incidental P losses in runoff studies (Smith et al., 2001b; Elliot et al, 2005; Torbert et al., 2005; Brennan et al., 2011b), but little attention has been given to the effect of chemical amendments on short and long-term nutrient availability to plants. In the US, where chemical amendment of poultry litter is a BMP, Moore and Edwards (2005) and Moore and Edwards (2007) reported results from a 20-year study, which began in 1995 and examined the effects of chemical amendment of poultry litter on soil productivity and water quality. They found that long-term land application of alum-amended poultry litter did not acidify soil in the same way as NH_4-N fertilizers, long-term P losses were reduced, and Al availability was lower from plots receiving alum-treated poultry manure than NH_4-N fertilizer.

With the exception of Kalbasi and Karthikeyan (2004), there has been little research on the effect of land spreading of chemically amended dairy cattle slurry to soil. Kalbasi and Karthikeyan

(2004) examined three silt loam soils with different STPs (12, 66 and 94 mg kg^{-1} Bray-1 P, respectively) in an incubation experiment conducted over a 24-mo period. Kalbasi and Karthikeyan (2004) found that alum and ferric chloride had no effect on soil pH, while lime increased soil pH slightly. This was consistent with the findings of the present study. These results were also consistent with another study by Brennan et al. (unpublished data). In that study, 5 soils, including soil taken from the same study site as the present study, were amended with chemical amendments and incubated for 9 months. While chemical amendments consistently reduced WEP, the STP and soil pH were not significantly affected by application of amended slurry, with the exception of $FeCl_3$-amended slurry in some instances. Due to the relatively short duration of the present study, it was not possible to examine the relationship between the STP of incubated soils and the *in-situ* STP when subject to a similar treatment.

4.4 Management implications of using chemically amended dairy slurry

Ireland has committed to meeting the requirements of the WFD to achieve at least ‘good status’ of all surface and groundwater by 2015. While current practices are effective, there will be a time-lag before current changes in farming practices will result in an observable reduction in nutrient losses and a reduction in risk to water quality. The time-lag will be site-specific and while it is likely that in many areas the effects will be shown relatively quickly, there may be a need for some new P mitigation measures. Results show that chemical amendments can significantly reduce P losses and that a once-off application of any of the chemical amendments examined will not result in a significant change in soil physical and chemical properties. It is, however, critical that the long-term effect of repeated applications of chemical amendments to slurry on STP, soil pH, soil WEP, soil microbiology and macro-biology be examined.

5. Conclusions

The findings of this study validate findings at laboratory-scale, with amendment of dairy cattle slurry with alum and PAC reducing DRP and TP losses (FWMC and loads) compared to the study-control. Alum was the most effective amendment at reducing PP and TP losses, while PAC was the most effective at reducing DRP losses. This study also showed that chemical amendment of dairy cattle slurry with alum increased NH_4-N loss (FWMC and loads) to runoff, while PAC reduced NH_4-N losses. Future work must examine the effects of chemical amendment of dairy cattle slurry on the N cycle and gaseous emissions. In addition, these results indicate that amendments may affect runoff volume for events occurring 48 hr after slurry application. Following from this study, the next step will be to examine the targeted use of chemical amendments at field and catchment-scale. In future, farm nutrient management must focus on examining all farms within a catchment and identifying areas which pose the greatest risk. It is possible that P mitigating methods, such as chemical amendment of dairy cattle slurry, may be used strategically within a catchment to bind P in cow and pig slurries. This work highlights the importance of considering both P and N losses when implementing a specific nutrient mitigation measure.

Acknowledgments

The first author gratefully acknowledges the award of a Walsh Fellowship by Teagasc to support this study. The authors are also grateful for assistance provided by Teagasc and NUI Galway staff and colleagues with special mention to Peter Fahy, Theresa Cowman, Carmel O’Connor, Denis Brennan, Linda Finn, Paddy Sills, Pat Donnelly, Stan Lalor, Nyncke Hoekstra and Paddy Hayes. The authors would also like to thank Michael Brennan for his assistance with fieldwork.

References

Alaoui A, Caduff U, Gerke HH, Weingartner R. Preferential flow effects on infiltration and runoff in grassland and forest soils. Vadose Zone J 2011; 10: 367-377.

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

APHA.Standard methods for the examination of water and wastewater. American Public Health Association (APHA). Washington: APHA; 2005.

Bowyer-Bower TAS, Burt TP. Rainfall simulators for investigating soil response to rainfall. Soil Technol 1989; 2: 1-16.

Brennan RB, Fenton O, Rodgers M, Healy MG. Evaluation of chemical amendments to control phosphorus losses from dairy slurry. Soil Use Manage 2011a; 27: 238-246.

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

British Standards. British standard methods of test for soils for civil engineering purposes. Determination of particle size distribution. BS 1377:1990:2. BSI, London., 1990.

Buda AR, Kleinman PJ, Bryant RB, Feyereisen GW. Effects of hydrology and field management on phosphorus transport in surface runoff. J Environ Qual 2009; 38: 2273-2284.

Byrne E. Chemical analysis of agricultural materials – methods used at Johnstown Castle Research Centre, Wexford. Published by AnForasTaluntais, 1979.

Correll DL. The role of phosphorus in the eutrophication of receiving waters: a review. J Environ Qual 1998; 27: 261-266.

Coulter BS, Lalor S. Major and micro nutrient advice for productive agricultural crops. Third Edition Teagasc Johnstown Castle Wexford.116 pp., 2008.

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

Dao TH, Cavigelli MA. Mineralizable carbon, nitrogen, and water-extractable phosphorus release from stockpiled and composted manure and manure-amended soils. Agron J 2003; 95: 405-413.

Dao TH, Daniel TC. Particulate and dissolved phosphorus chemical separation and phosphorus release from treated dairy manure. J Environ Qual 2002; 31: 1388-1398.

Dou Z, Zhang GY, Stout WL, Toth JD, Ferguson JD. Efficacy of alum and coal combustion by-products in stabilizing manure phosphorus. J Environ Qual 2003;32:1490–7.

Elliott H, Brandt R, O'Connor GA. Runoff phosphorus losses from surface-applied biosolids. J Environ Qual 2005; 34: 1632-1639.

Fenton O, Healy MG, Brennan RB, Serrenho A, Lalor STJ, O hUallacháin D, Richards KG. 2011. Agricultural wastewaters. Chapter 22. pp. 447-470. Fernando Sebastián García Einschlag (Ed.) In: Waste Water - Evaluation and Management. IN-TECH Publishers, Vienna. ISBN: 978-953-307-233-3.

Hanrahan LP, Jokela WE, Knapp JR. Dairy diet phosphorus and rainfall timing effects on runoff phosphorus from land-applied manure. J Environ Qual 2009; 38: 212-217.

Hudnell HK. The state of US freshwater harmful algal blooms assessments, policy and legislation.Toxicon 2010; 55:1024-1034.

Johnes PJ, Foy R, Butterfield D, Haygarth PM. Land use for England and Wales: Evaluation of management options to support 'good ecological status' in surface freshwaters. Soil Use Manage 2007; 23: 176-196.

Kalbasi M, Karthikeyan KG. Phosphorus dynamics in soils receiving chemically treated dairy manure. J Environ Qual 2004; 33: 2296-2305.

Kleinman PJA, Sharpley AN. Effect of broadcast manure on runoff phosphorus concentrations over successive rainfall events. J Environ Qual 2003; 32: 1072-1081.

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

Kleinman PJA, Sullivan D, Wolf A, Brandt R, Dou Z, Elliott H, Kovar J, Leytem A, Maguire R, Moore P, Saporito L, Sharpley AN, Shober A, Sims T, Toth J, Toor G, Zhang H. Selection of a water extractable phosphorus test for manures and biosolids as an indicator of runoff loss potential. J Environ Qual 2007; 36: 1357-1367.

Kramers G, Richards KG, Holden NM. Assessing the potential for the occurrence and character of preferential flow in three Irish grassland soils using image analysis. Geoderma 2009; 153: 362-371.

Kurz I, O'Reilly CD, Tunney H. Impact of cattle on soil physical properties and nutrient concentrations in overland flow from pasture in Ireland. AgrEcosyst Environ 2006; 113: 378-390.

Lefcourt AM, Meisinger JJ. Effect of adding alum or zeolite to dairy slurry on ammonia volatilization and chemical composition. J Dairy Sci 2001, 84, 1814-1821.

McDowell R, Sharpley A.N. Phosphorus transport in overland flow in response to position of manure application. J Environ Qual 2002; 31: 217-227.

Moore PA, Edwards DR. Long-term effects of poultry litter, alum-treated litter and ammonium nitrate on aluminum availability in soils. J Environ Qual 2005; 34: 2104-2111.

Moore PA, Edwards DR. Long-term effects of poultry litter, alum-treated litter, and ammonium nitrate on phosphorus availability in soils. J Environ Qual 2007; 36:163–174.

Morgan MF. Chemical soil diagnosis by the Universal Soil Testing System. Connecticut. Connecticut agricultural Experimental Station Bulletin 450 Connecticut. New Haven, 1941.

Norbiato D, Borga M, Merz R, Blöschl G, Carton A. Controls on event runoff coefficients in the eastern Italian Alps. J Hydrol 2009; 375: 312-325.

Núñez-Delgado A, López-Periago E, Quiroga-Lago A, Díaz-FierrosViqueira F. Surface runoff pollution by cattle slurry and inorganic fertilizer spreading: chemical oxygen demand, ortho-phosphates, and electrical conductivity levels for different buffer strip lengths. Wat Sci Technol 2001;44:173–180.

O'Rourke SM, Foy RH, Watson CJ, Ferris CP, Gordon A. Effect of varying the phosphorus content of dairy cow diets on losses of phosphorus in overland flow following surface applications of manure. J Environ Qual 2010; 39: 2138-2146.

OJEC, Official Journal of the European Communities. Directive 2000/60/EC of the European Parliament and of the council of 23 October 2000 establishing a framework for Community action in the field of water policy. 2000.

Paerl HW. Nutrient and other environmental controls of harmful cyanobacterial blooms along the freshwater-marine continuum.pp. 218-237. In: H.K. Hundell, editor, Cyanobacterial harmful algal blooms: State of the science and research needs. Springer Press, New York, NY. 2008.

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

Pote DH, Reed BA, Daniel TC, Nichols DJ, Moore PA, Edwards DR, et al. Water-Quality effects of infiltration rate and manure application rate for soils receiving swine manure. J Soil Water Conserv 2001; 56: 32-37.

Preedy N, McTiernan K, Matthews R, Heathwaite L, Haygarth P. Rapid incidental phosphorus transfers from grassland. J Environ Qual 2001; 30: 2105-12.

Roth CH, Pavan MA. Effects of and gypsum on clay dispersion and infiltration in samples of a Brazilian oxisoil. Geoderma 1991; 48: 351-361.

Ryan M, Fanning A. Effects of fertilizer N and slurry on nitrate leaching ‘lysimeter studies on 5 soils’. Irish Geog 1996; 29: 126-136.

SAS. SAS for windows.Version 9.1.SAS/STAT® User’s Guide. Cary, NC. SAS Institute Inc., 2004.

Schindler DW, Hecky RE, Findlay DL, Stainton MP, Parker BR, Paterson MJ, Beaty KG, Lyng M, Kasian SE. Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment. Proc Natl Acad Sci2008: 105(32): 11254-11258.

Schulte RPO, Diamond J, Finkele K, Holden NM, Brereton AJ. Predicting the soil moisture conditions of Irish grasslands. Irish J Agr Food Res 2005; 44: 95-110.

Sharpley AN, Daniel TC, Gibson G, Bundy L, Cabrera M, Sims T, Stevens R, Lemunyon J, Kleinman PJA, Parry R. Best management practices to minimize agricultural phosphorus impacts on water quality. USDA-ARS Publication. 163. U.S. Govt. Printing Office, Washington, DC. 2006.

SERA-17 (Southern Exchange-Research Activity).Treating swine manure with aluminum chloride. Available at http://www.sera17.ext.vt.edu/SERA_17_Publications.htm. 2012.

Smith KA, Jackson DR, Pepper TJ. Nutrient losses by surface run-off following the application of organic manures to arable land. 1. Nitrogen. Environ Pollut2001a; 112: 41-51.

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

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

Stevens CJ, Quinton JN. Policy implications of pollution swapping. Phys Chem Earth Parts A/B/C 2009; 34(8–9):589–94.

Tarchitzky J, Chen Y, Banin A. Humic substances and pH effects on sodium-and calcium-montmorillonite flocculation and dispersion. Soil Sci Soc Am 1993; 57: 367-372.

Torbert HA, King KW, Harmel RD. Impact of soil amendments on reducing phosphorus losses from runoff in sod. J Environ Qual 2005; 34: 1415-1421.

USDA-NRCS (Natural Resources Conservation Service).Amendments for treatment of agricultural wastes.Conservation Practice Standard 591 - http://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs143_026499.pdf.Available at http://www.nrcs.usda.gov/wps/portal/nrcs/detailfull/national/technical/cp/ncps/?&cid=nrcs143_026849. 2012.

Vitousek PM, Naylor R, Crews T, David MB, Drinkwater LE, Holland E, Johnes P J, Katzenberger J, Martinelli LA, Matson PA, Nziguheba G, Ojima D, Palm CA, Robertson GP, Sanchez PA, Townsend AR, Zhang FS. Nutrient imbalances in agricultural development. Science 2009; 324: 1519-1520.

Wainwright J, Parsons AJ. The effect of temporal variations in rainfall on scale dependency in runoff coefficients. Wat Resour Res 2002; 38: 1271-1281.

Withers PJA, Bailey GA. Sediment and phosphorus transfer in overland flow from a maize field receiving manure. Soil Use Manage 2003; 19: 28-35.

Zhang Y, Liu BY, Zhang QC, Xie Y. Effect of different vegetation types on soil erosion by water.Acta Bot Sin 2003: 1204-1209.

Table 1 Soil pH, Morgan's extractable P, K and Mg, sand silt, clay factions, textural class of soil within 0.6 ha plot.

Position	Piezometer No.[1]	pH	Morgan's P mg L^{-1}	P index[2]	K mg L^{-1}	Mg mg L^{-1}	Sand %	Silt %	Clay %	Textural Class
Lower	1	5.8	2.6	2	173	171	52	30	18	Sandy Loam
Middle	2	5.9	3.2	3	140	195	47	36	18	Sandy Silt Loam
Upper	3	6.1	3.6	3	96	151	44	36	21	Clay Loam
Average		5.9	3.1		136	172	47.7	34.0	19.0	
Stddev		0.2	0.5		38.6	22	4	3.5	1.7	

[1] The location of the piezometers is illustrated in Fig 1.

[2] P Index 2 expects a likely response to fertilizers whereas a P index of 3 expects a tenuous or unlikely response.

Table 2 Slurry DM, pH, water extractable phosphorus (WEP), total nitrogen (TN), total phosphorus (TP) and total potassium (TK) and average concentrations of NH_4-N (n=5).

Treatment	DM	pH	WEP g kg^{-1}	TN mg L^{-1}	TP mg L^{-1}	TK mg L^{-1}	NH_4^+-N mg L^{-1}
Slurry (control)	9.1 (0.54)	7.1 (0.62)	3.19 (0.37)	3960 (741)	1240 (145)	5170 (870)	1200 (260)
Alum	9.6 (0.58	6.5 (0.44)	0.003(0.001)	4410 (590)	1260 (190)	5210 (640)	1160 (270)
PAC	9.42 (0.64)	6.9 (0.47)	0.007 (0.008)	3980 (1280)	1200 (270)	4330 (1290)	1180 (290)
Lime	9.4 (0.38)	8.8 (0.67)	2.48 (0.99)	5010 (725)	1390 (150)	5610 (840)	1210 (300)
Average	9.38	7.325	1.4	4340	1270	5080	1190
Stddev	0.2	1.01	1.7	492	82.2	538	22.2

Table 3 The average slope, soil pH, soil water extractable P (WEP), Morgan's extractable P, potassium (K), magnesium (Mg) and lime requirement (LR) on the day before the experiment (t_0) and after the experiment (t_{30}) for all of the treatments.

Treatment	Slope	pH_0/pH_{30}	WEP_0/WEP_{30}	P_0/P_{30}	K_0/K_{30}	Mg_0/Mg_{30}	LR_0/LR_{30}
	%		mgkg^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
Soil	3.05	5.97/5.97	4.13/6.32	5.78/3.86	57.9/93.4	182/180	4.88/4.38
Slurry (control)	2.90	5.82/5.97	8.11/4.78	6.31/8.98	56.8/91.0	173/186	6.00/4.20
Alum	4.38	5.92/5.83	6.17/6.77	5.03/5.26	52.9/66.9	194/192	5.30/5.00
Lime	3.75	6.06/6.04	8.82/9.71	6.82/11.22	59.1/80.0	188/199	4.20/3.80
PAC	3.68	5.93/6.11	6.99/5/17	6.99/5.12	58.6/93.7	160/193	5.10/3.30

Fig 1 Map of study site showing ground elevation, topography, slope, soil conductivity, groundwater flow direction, location of subplots, piezometers and diagram of runoff collection channel and plot isolation.

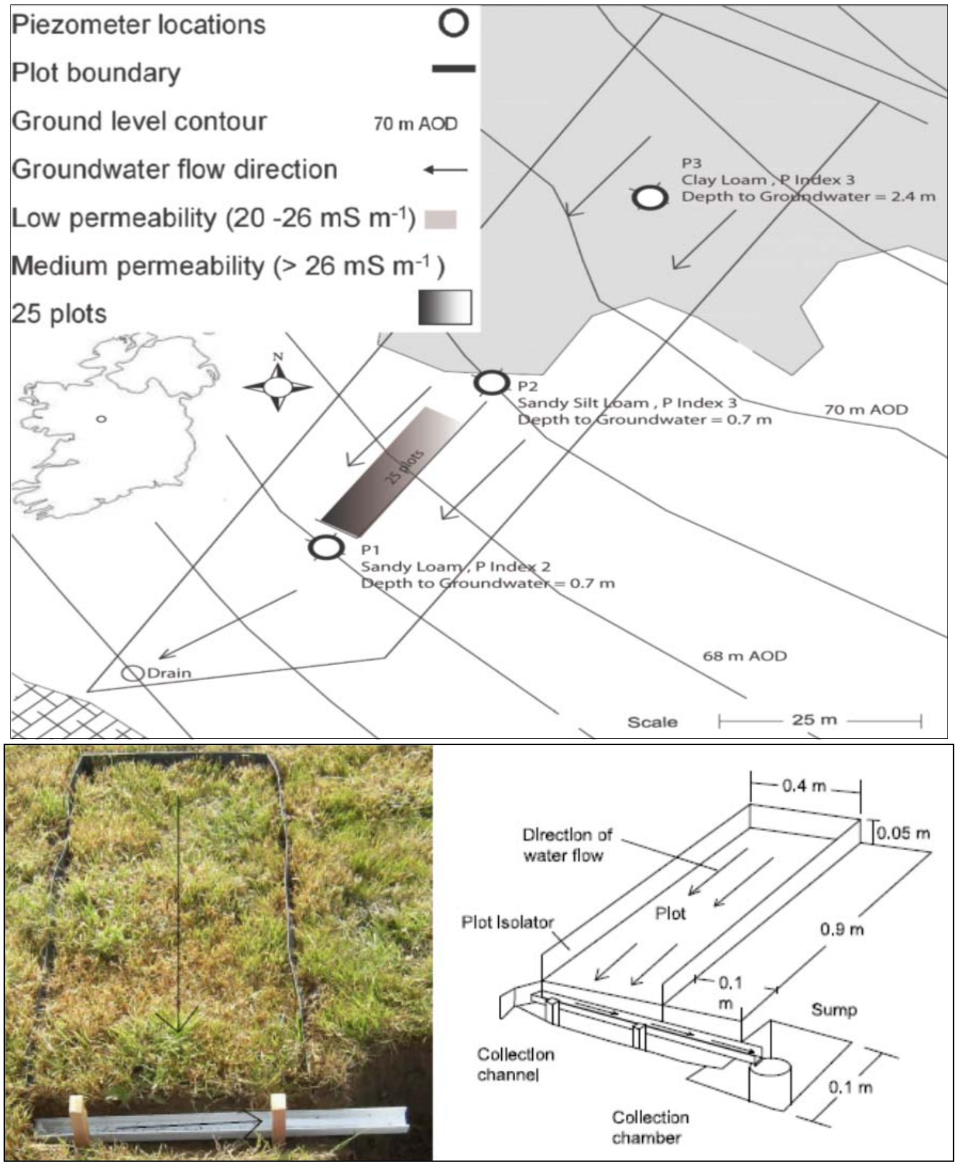


Fig 2 Measured daily rainfall (mm) and simulated soil moisture deficit (SMD) for well, moderate and poorly drained soils. Rainfall applied to plots during RS1-3 is added to measured daily rainfall and used for simulated SMD calculation. X axis is in Julian Days.

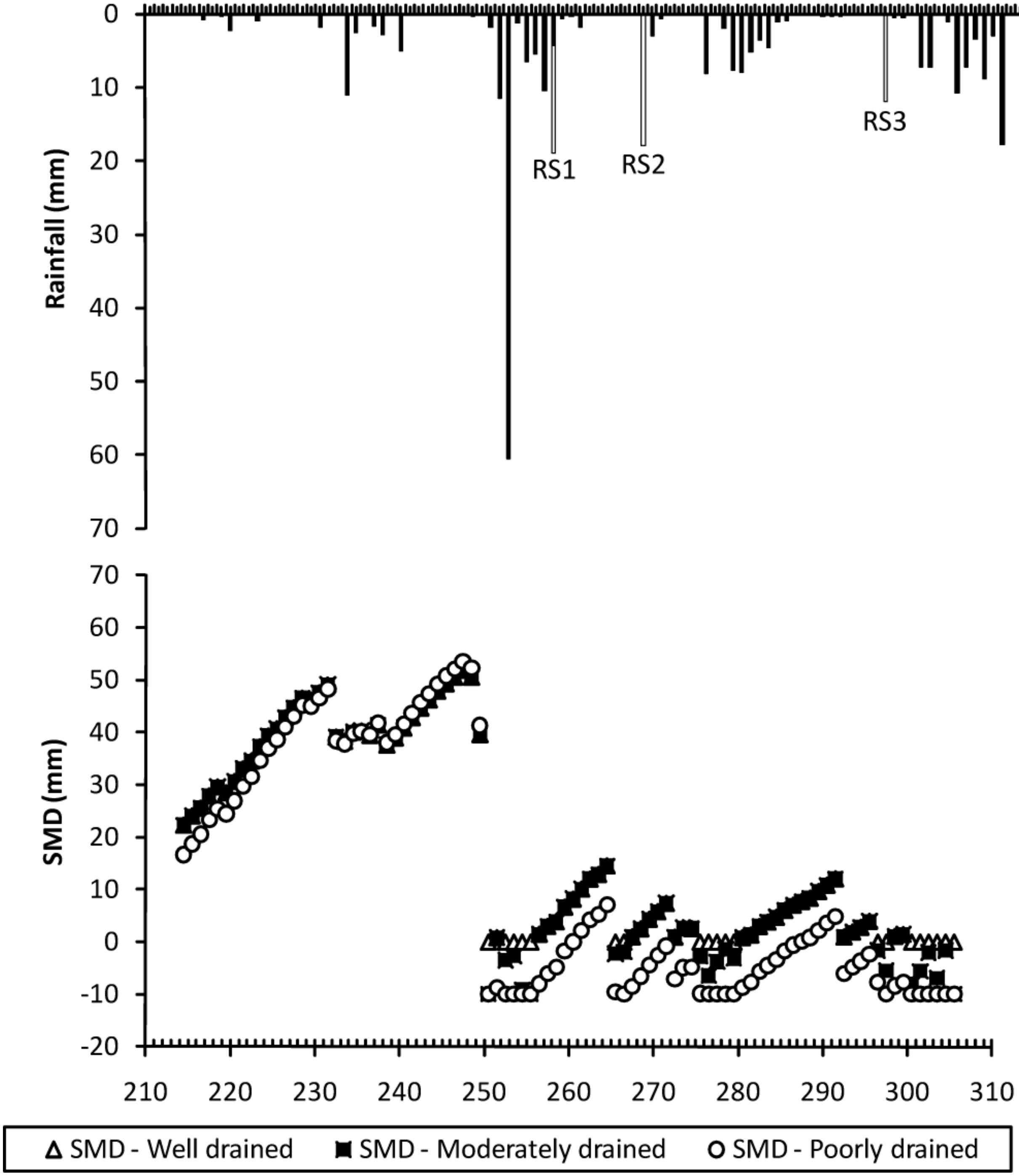


Fig 3 Flow-weighted mean concentration and total loads of particulate phosphorus (PP), dissolved un-reactive phosphorus (DUP) and dissolved reactive phosphorus (DRP).

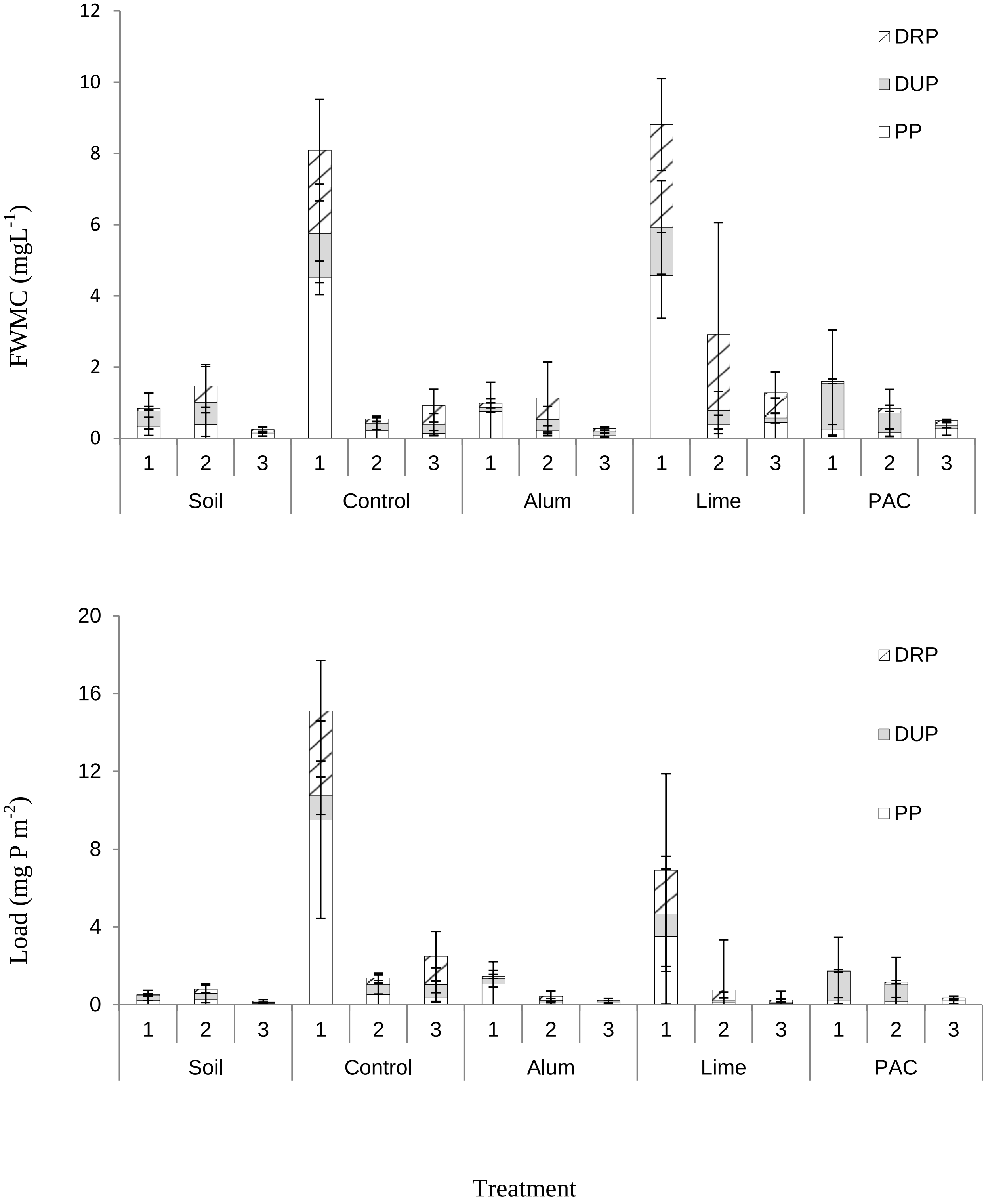


Fig 4 Flow-weighted mean concentration and total loads of nitrate (NO_3-N) and ammonium (NH_4-N).

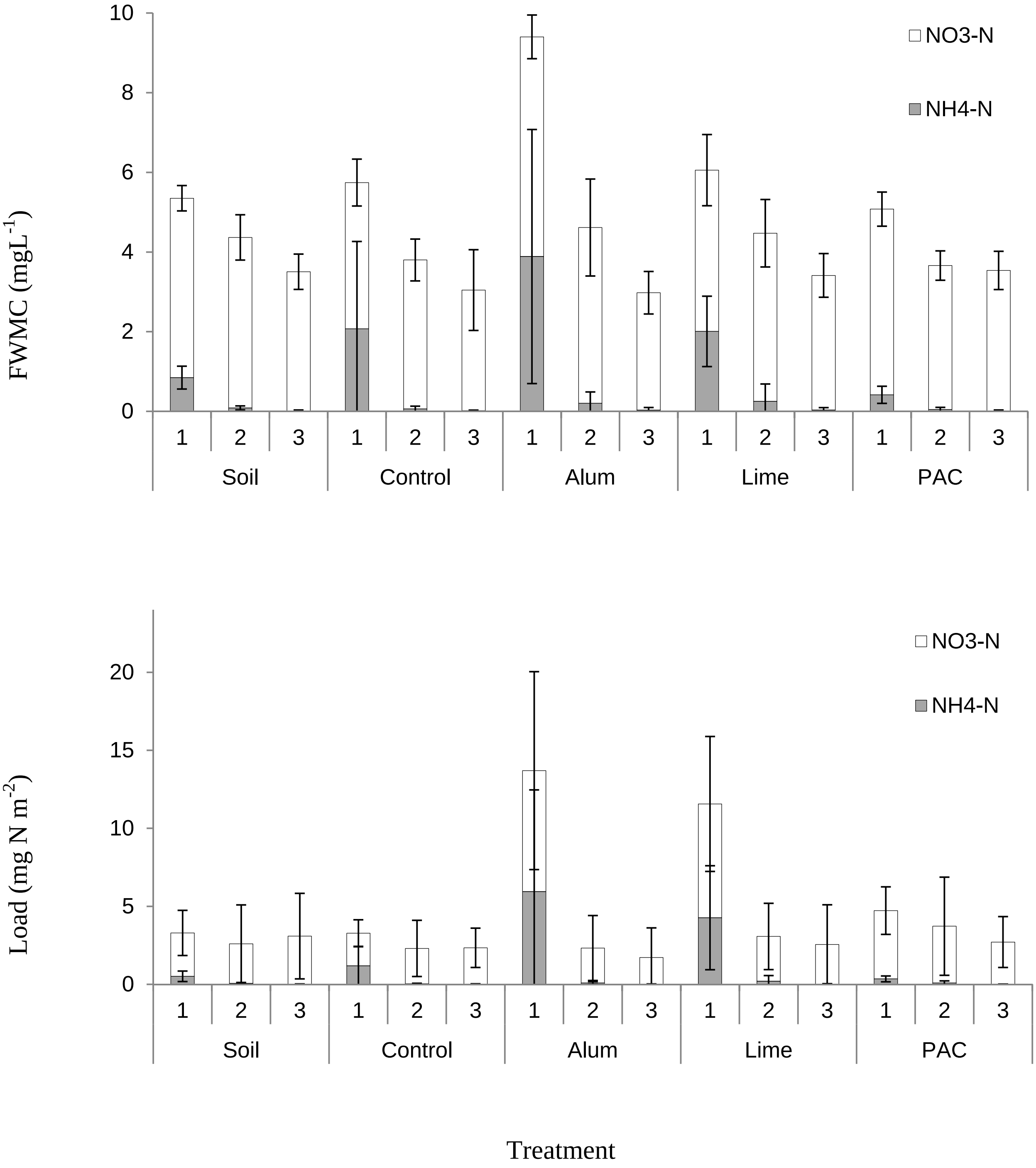
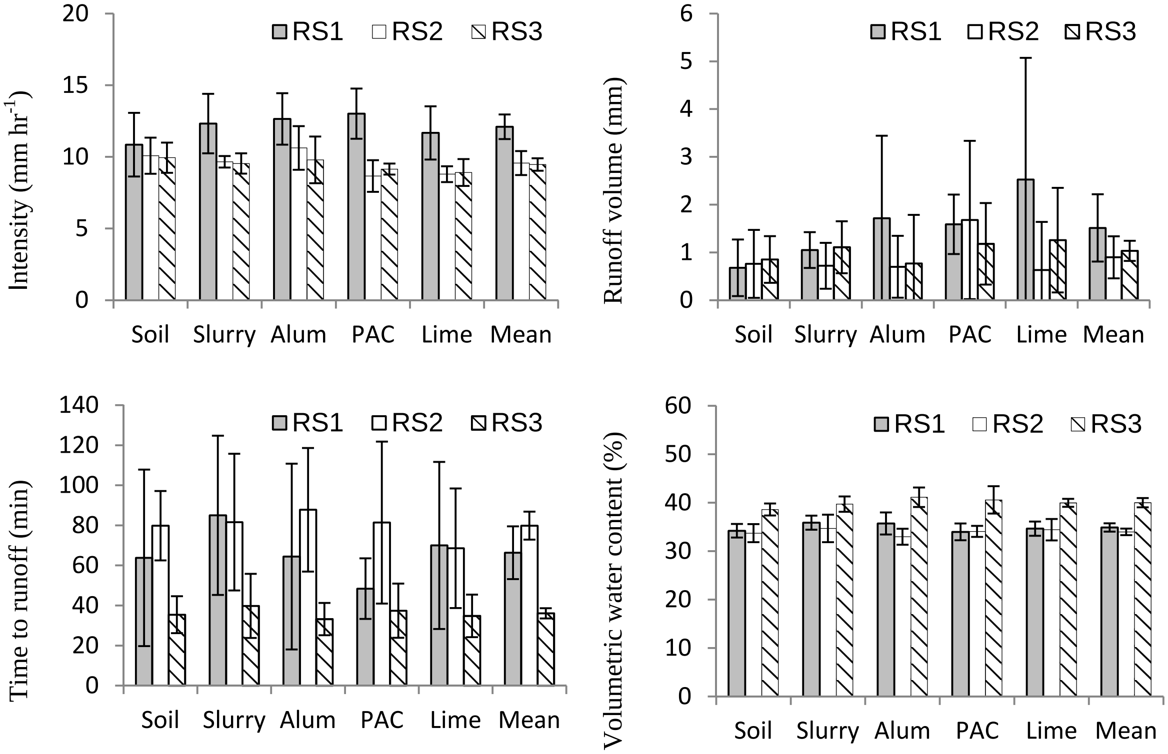


Fig 5 Average rainfall intensity, runoff volume, time to runoff and soil volumetric water content for the first (RS1), second (RS2) and third (RS3) rainfall events.



Mean (average value for all plots)