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# Use of zeolite with alum and PAC amendments to mitigate runoff losses of P, N and suspended solids from agricultural wastes applied to grassed soils

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**Abbreviation list:**

DSW – Dairy soiled water

PAC – Poly-aluminum chloride

FWMC – Flow-weighted mean concentration

DRP – Dissolved reactive phosphorus

## Abstract

Diffuse pollutant losses containing phosphorus (P), nitrogen (N) and suspended solids (SS) can occur when agricultural wastes are applied to soil. This study aimed to mitigate P, N and SS losses in runoff from grassed soils, onto which three types of agricultural wastes, dairy slurry, pig slurry and dairy soiled water (DSW), were applied by combining amendments of either zeolite and poly-aluminum chloride (PAC) with dairy and pig slurries, or zeolite and alum with DSW. Four treatments were investigated in rainfall simulation studies: (1) control soil (2) agricultural wastes (3) dairy and pig slurries amended with PAC; DSW amended with alum, and (4) dairy and pig slurries amended with zeolite and PAC; DSW amended with zeolite and alum. Our data showed that combined amendments of zeolite and PAC applied to dairy and pig slurries reduced total phosphorus (TP) in runoff by 87% and 81%, respectively, compared to unamended slurries. A combined amendment of zeolite and alum applied to DSW reduced TP in runoff by 50% compared to unamended DSW. The corresponding reductions in total nitrogen (TN) were 56% for dairy slurry and 45% for both pig slurry and DSW. Use of combined amendments reduced SS in runoff by 73% and 44% for dairy and pig slurries, and 25% for DSW compared to unamended controls, but were not significantly different from those using chemical amendments only. The findings of this study are that combined amendments of zeolite and either PAC or alum reduce TP and TN losses in runoff to a greater extent than use of single PAC or alum amendments, and are most effective when used with dairy slurry and pig slurry but less effective when used with DSW.

*Keywords:* agricultural wastes, zeolite, poly-aluminum chloride, alum, phosphorus, nitrogen, suspended solids, runoff.

## 1. Introduction

Excessive application of agricultural waste to soils may have environmental impacts, including phosphorus (P), nitrogen (N) and suspended solids (SS) losses, and increase greenhouse gas emissions (Smith et al., 2001a; Chadwick et al., 2011; Kröger et al., 2013; McDowell and Hamilton, 2013). Loss of P, N and SS in overland flow is affected by the time interval between surface application and rainfall events (Allen and Mallarino, 2008; Hanrahan et al., 2009), antecedent hydrologic conditions (Brennan et al., 2012), flow path length (McDowell and Sharpley, 2002), surface slope (Alaoui et al., 2011), soil type (Wall et al., 2013), and the short and long-term effects of agricultural waste application to the soil structure (McDowell et al., 2004). Event P losses in surface runoff following land application of agricultural wastes may be dominated by particulate phosphorus (PP) (Preedy et al., 2001) or by dissolved phosphorus, depending on individual circumstances such as grazing animals, type of stock, topography and degree of exposure of the soil to rainfall events (Hart et al., 2004), while most of the permanent P losses in surface runoff from soils are in dissolved form (Heathwaite and Dils, 2000). Nitrogen losses are dominated by ammonium ($NH_4$-N) (Heathwaite et al., 1996; Smith et al., 2001a). Suspended sediment is an important carrier of contaminants (Quinton and Catt, 2007) and, depending on the soil type and rainfall characteristics, P enriched soil particles may increase the proportion of PP in surface runoff (McDowell et al., 2001; Miller et al., 2009).

With European policy advocating farm intensification (Department of Agriculture, Food and the Marine, 2013), farmers may have no choice but to spread agricultural waste on land with a high soil P. Land spreading remains the most economical and widespread disposal practice for agricultural wastes (e.g. Nolan et al., 2012). Use of chemical amendments applied to agricultural waste to reduce P losses in surface runoff following land application has been shown to be effective (Smith et al., 2001b; Kalbasi and Karthikeyan, 2004; Moore and Edwards, 2007). In contrast to most studies, Brennan et al. (2012) tested the effect of either poly-aluminum chloride (PAC; $Aln(OH)mCl_3n\text{-}m$; 10% $Al_2O_3$), alum ($Al_2(SO_4)_3 \cdot nH_2O$; 8% $Al_2O_3$), or lime ($Ca(OH)_2$) on both P and N losses. They found that the three chemicals did not have a significant effect on N losses following the first rainfall event two days after slurry application to grassed plots.

Zeolite has been shown to be effective in adsorbing N from synthetic wastes (Englert and Rubio, 2005; Widiastuti et al., 2011) and agricultural wastes (Nguyen and Tanner, 1998). Nguyen and Tanner (1998) found that two types of New Zealand zeolite (clinoptilolite and modernite) removed 62-99% of N in batch adsorption experiments using domestic sewage and synthetic, pig and dairy wastewaters. They found in an infiltration experiment that for a throughput of up to 40 bed volumes, the removal rate of $NH_4$-N from pig and dairy slurries was over 98% at a hydraulic loading rate (HLR) of 0.47 mm $min^{-1}$ and 50-90% at a HLR of 15.9 mm $min^{-1}$. Zeolite has also been shown to be effective in reducing ammonia emissions from dairy slurry stored in the holding pit of a 100-cow free stall barn (Meisinger et al., 2001).

To date no study has assessed the effectiveness of zeolite, used predominantly for N removal, in combination with chemical amendments, used predominantly for P and SS removal, to mitigate P, N and SS losses in surface runoff from land applied agricultural wastes. The objectives of this study were to investigate if zeolite, in combination with PAC for dairy and pig slurries and alum for dairy soiled water (DSW), was effective in reducing event losses of P, N and SS from grassed soil in a laboratory scale rainfall simulation study.

## 2. Materials and Methods

### 2.1 Chemical and physical analyses

### 2.1.1 Agricultural wastes

Total phosphorus (TP) was measured using acid persulphate digestion and dissolved reactive phosphorus (DRP) by centrifuging at 17,970 RCF (relative centrifugal force) for 5 min, filtering through 0.45 µm filters and measuring colorimetrically using a nutrient analyzer (Konelab 20, Thermo Clinical Laboratories Systems, Finland). Total nitrogen (TN) was measured using a BioTector TOC TN TP Analyzer (BioTector Analytical Systems Ltd., Cork, Ireland). Ammonium was extracted from fresh waste by shaking 10 g of 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. Waste pH was measured using a pH probe (WTW, Germany) and dry matter (DM) was measured by drying at 105 °C for 24 h. All parameters were tested in accordance with the standard methods (APHA, 2005).

### 2.1.2 Zeolite

The zeolite was sieved to a particle size of 2.36 – 3.35 mm and analyzed for $Al_2O_3$, BaO, $Fe_2O_3$, MnO, $TiO_2$, and SrO using inductively coupled plasma mass spectrometry (ICP-MS), CaO, MgO, $K_2O$ and Na2O using atomic adsorption spectrometry (AAS), $P_2O_5$ by colorimetry and $SiO_2$ by method of fusion (Vogel, 1989).

### 2.1.3 Soil

Soil phosphorus was measured by air drying soil cores (n=3) at 40 °C for 72 h, crushing to pass a 2 mm sieve, and testing for Morgan's Phosphorus (Pm) using Morgan's extracting solution (Morgan, 1941). Soil pH was measured in triplicate using a pH probe and a 2:1 ratio of deionized water to soil (Thomas, 1996). Particle size distribution was determined in accordance with BS 1377-2 (BSI, 1990a) and the organic content of the soil was determined using the loss of ignition test in accordance with BS1377-3 (BSI, 1990b). Water extractable phosphorus (WEP) was measured by shaking 1 g of fresh soil in 100 mL of deionized water for 30 min, filtering the supernatant water through 0.45 μm filter paper, and measuring the P colorimetrically.

### 2.1.4 Rainfall simulator runoff

Runoff samples were tested for pH using a pH probe and for SS using vacuum filtration of at least 50 mL of well-mixed, previously unfiltered, subsamples through Whatman GF/C (pore size 1.2 μm) filter paper (APHA, 2005). Sub-samples were filtered through 0.45 μm filters and measured colorimetrically for DRP, $NH_4$-N, total oxidized nitrogen (TON) and nitrite-N ($NO_2$–N) using a nutrient analyzer (Konelab 20, Thermo Clinical Labsystems, Finland). Unfiltered sub-samples were tested for TP and total dissolved phosphorus (TDP) using acid persulphate digestion, and for TN using a BioTector Analyzer (BioTector Analytical Systems Ltd., Cork, Ireland).

## 2.2 Materials collection and characterization

### 2.2.1 Agricultural wastes

Three types of agricultural wastes were collected from the Teagasc Research Centre, Moorepark, Fermoy, Co. Cork. They were: (1) dairy slurry, from a slatted unit housing dairy cows (2) pig slurry, from an integrated pig unit and (3) DSW from a milking parlor washwater collection sump. Dairy soiled water is defined as dairy wash water from hard standing farmyard areas contaminated with livestock feces, urine or silage effluent, fertilizers and parlor washings, which have a DM content < 1% and a 5-day biochemical oxygen demand ($BOD_5$) < 2,500 mg $L^{-1}$. All wastes were homogenized immediately prior to collection by agitating for 30 min using mechanical agitators. The samples were stored in 25 L containers, which were placed in a temperature-controlled room at 11 °C for 12 h prior to the experimental onset. Triplicate samples of each waste were tested for TP, DRP, TN, $NH_4$-N, pH and DM (Table 1).

### 2.2.2 Zeolite

The zeolite used in this study was of Turkish origin and the sieved zeolite (2.36 – 3.35 mm), comprised mainly silica (66.7% $SiO_2$) and aluminum (10.4% $Al_2O_3$) (Table 2).

### 2.2.3 Soil

Intact grassed soil samples, 500 mm long, 300 mm wide and 100 mm deep, were collected from grassland, which had not received fertilizer application for more than

10 yr, in Galway City, Republic of Ireland. The soil was a poorly drained sandy loam (57±5% sand, 29±4% silt and 14±2% clay) with a Pm of 2.8 ±0.5 mg kg$^{-1}$ (mg P L$^{-1}$), a WEP of 2.3±0.4 mg P kg$^{-1}$, a pH of 6.4±0.3 and an organic matter content of 5±2%. The soil type is classified as an acid brown earth Cambisol (WRB classification).

### 2.3 Adsorption capacity of zeolite

The ability of zeolite to remove P ($PO_4$-P) and N ($NH_4$-N) from the three types of wastes was first investigated using a multi-point Langmuir isotherm (McBride, 2000):

$$\frac{C_e}{\frac{x}{m}} = \frac{1}{ab} + \frac{C_e}{b} \quad (1)$$

where $C_e$ is the concentration of P or N in solution at equilibrium (mg L$^{-1}$), x/m is the mass of P or N adsorbed per unit mass of amendments (g kg$^{-1}$) at $C_e$, $a$ is a constant related to the binding strength of molecules onto the amendments, and $b$ is the theoretical amount of P or N adsorbed to form a complete monolayer on the surface. This provided an estimate of the maximum adsorption capacity of the zeolite (g kg$^{-1}$).

Zeolite was sieved (n=3) to a particle size 2.36 - 3.35 mm and 4 g placed in 100 mL capacity containers and overlain by 40 mL of raw and various dilutions (1/2, 1/4, 1/6 and 1/10 by volume) of each waste type. All containers were sealed and placed on a reciprocating shaker for 24 h at 250 rpm. On removal from the shaker, the samples were allowed to settle for 1 h and a subsample of the settled mixture was centrifuged at 17,970 RCF for 5 min. The supernatant was removed, filtered, and measured for DRP. Ammonium was measured by extraction and wastes with DM > 1% were measured for WEP to establish P availability in runoff (Kleinman et al., 2007).

## 2.4 Optimum zeolite application

Bench-scale tests were used to establish optimum application ratios of zeolite (expressed as g zeolite per g DM of waste) for $NH_4$-N removal for each of the wastes. Sieved zeolite (2.36 – 3.35 mm) was added (n=3) in amounts ranging from 1 to 15 g to 40 mL of each waste type in 100 mL containers. All containers were sealed and placed on a reciprocating shaker for 24 h at 250 rpm. The samples were then allowed to settle for 1 h, centrifuged at 17,970 RCF for 5 min and tested for $NH_4$-N by adding 25 mL of the supernatant to 500 mL of 0.1M HCL, shaking for 30 min at 200 rpm, filtering through 0.45 µm filter paper and measuring colorimetrically. The optimum application ratio was defined as the mass of zeolite above which there was little or no enhanced rate of $NH_4$-N removal in the supernatant, or where the volume of zeolite comprised no greater than 10% of the volume of waste.

To reduce WEP, the following chemicals were mixed with the wastes to which zeolite had been applied at the established optimum ratios for $NH_4$-N removal: (1) PAC comprising 10% $Al_2O_3$ to the dairy slurry at five Al:TP stoichiometric ratios between 0.5:1 and 1.5:1 (2) PAC comprising 10% $Al_2O_3$ to the pig slurry at five Al:TP stoichiometric ratios between 0.3:1 and 1.25:1; and (3) alum comprising $Al_2(SO_4)_3 \cdot 18H_2O$ to the DSW at five Al:TP stoichiometric ratios between 5:1 and 12:1. The combination of amendments that produced the best reductions of $NH_4$-N concentrations and WEP from the wastes were used in the runoff experiments.

## 2.5 Rainfall simulation study

Runoff experiments were conducted in triplicate comparing: (1) control soil (2) animal wastes (3) DSW amended with alum; dairy and pig slurries amended with

PAC (4) DSW amended with zeolite and alum; dairy and pig slurries amended with zeolite and PAC. Zeolite was applied at ratios of 2 g $g^{-1}$ DM to the dairy slurry, 6 g $g^{-1}$ DM to the pig slurry and 10 g $g^{-1}$ DM to the DSW. PAC was added at stoichiometric ratios of 1.25:1 to the dairy slurry and 1:1 Al:TP to the pig slurry. Alum was added at a stoichiometric ratio of 5:1 Al:TP to the DSW. The waste application rates were 19 kg TP $ha^{-1}$ for pig and dairy slurries and 50 $m^3$ $ha^{-1}$ for DSW, which equated to 31, 34 and 50 t $ha^{-1}$ for pig and dairy slurries and DSW, respectively. All wastes were mixed for 10 min at 200 rpm using a jar test flocculator and then applied by even and consistent hand spreading in repeated figure eight patterns to the grassed soil.

### 2.5.1 Runoff boxes and rainfall simulation

The rainfall simulator consisted of a single 1/4HH-SS14SQW nozzle (Spraying Systems Co. Wheaton, IL) attached to a 4.5 m high steel frame and calibrated to an intensity of 9.6 ±0.16 $mmh^{-1}$ and a droplet impact energy of 260 kJ $mm^{-1}$ $ha^{-1}$ at 80% intensity (Regan et al., 2010). Mains water supply used in the rainfall simulations had a DRP concentration of less than 0.005 mg $L^{-1}$, a pH of 7.7±0.2 and an electrical conductivity (measured using an LF 96 Conductivity Meter, WTW, Germany) of 0.435 dS $m^{-1}$.

This experiment used laboratory runoff boxes, 1 m long by 0.225 m wide by 0.05 m deep with side walls 25 mm higher than the soil surface and 5 mm diameter drainage holes each located at 0.3 m intervals along the base (Regan et al., 2010). The runoff boxes were positioned at a 10% slope to the horizontal, and all surface runoff was collected at the downstream end using an overflow weir with the crest positioned at the same level as the soil surface. Muslin cloth was placed at the base of each laboratory runoff box to prevent soil loss through the drain holes at the base before packing the soil. Intact grassed cores from the study site were transported to the laboratory and stored at 11 °C prior to testing. All experiments were carried out within 14 d of soil core collection. Immediately prior to the start of each runoff box experiment, each core was trimmed to a typical length of between 450-500 mm and butted against an adjacent core to form a continuous surface of between two and three cores. Molten candle wax was used to seal any gaps between the cores and the sides of the runoff box. The grass on the soil samples was cut to an approximate length of 25 mm to simulate freshly cut meadow conditions.

The drain holes at the base of each runoff box were initially plugged and the packed soil cores were then saturated using a rotating disc, variable-intensity rainfall simulator (Williams et al., 1998) until ponding occurred on the soil surface. The soil was then left to drain for 24 h to replicate field capacity conditions before the experiment commenced. At t = 24 h, the drain holes were sealed and remained so for the remainder of the experiment. At this point (t = 24 h), unamended wastes and wastes amended with either a combination of zeolite and PAC/alum amendment or PAC/alum amendment only, were spread on the soil and left for 48 h. At t = 72 h, 96 h and 120 h, successive rainfall events (RE1, RE2, RE3), with an intensity of approximately 10 mm $h^{-1}$, were applied to the same sod in each runoff box. Each event lasted for 30 min after continuous runoff was observed. Surface runoff samples for each event were collected at 5 min intervals over this 30 min period and tested immediately following each rainfall simulation.

### 2.5.2 Runoff analysis

Each of the samples taken at 5 min intervals was tested for pH and for SS. Sub-samples, also taken at 5 min intervals, were measured for DRP, $NH_4$-N, TON and $NO_2$–N. Nitrate-N was calculated by subtracting $NO_2$–N from TON. Unfiltered sub-samples, taken at 10, 20 and 30 min after continuous runoff were tested for TP, TDP and TN. Dissolved unreactive phosphorus (DUP) was calculated by subtracting DRP from TDP and PP was calculated by subtracting TDP from TP.

### 2.5.3 Data analysis

Flow-weighted mean concentrations (FWMCs) were determined for each rainfall simulation event and the data were analyzed using repeated measures ANOVA in SPSS (IBM SPSS Statistics 20 Core System). Logarithmic transformations were required for all variables to satisfy the normality assumption based on checking post-analysis residuals for normality and homogeneity of variance.

## 3. Results

### 3.1 Adsorption Capacity and bench scale studies

The monolayer adsorption capacity of zeolite, $q_{max}$, ranged from 0.06 (pig slurry) to 0.31 (dairy slurry) mg P $g^{-1}$ ($PO_4$-P) and from 0.74 (DSW) to 7.88 (pig slurry) mg N $g^{-1}$ ($NH_4$-N). The optimum combined amendment application rates for reduction of both $PO_4$-P and $NH_4$-N for dairy slurry were 2 g $g^{-1}$ DM of zeolite + a stoichiometric PAC ratio of 1.25:1 (Al:TP). The corresponding rates for pig slurry were 6 g $g^{-1}$ DM of zeolite + a stoichiometric PAC ratio of 1:1 (Al:TP) and for DSW, 10 g $g^{-1}$ DM of zeolite + a stoichiometric alum ratio of 5:1 (Al:TP).

## 3.2 Runoff from laboratory rainfall simulation study

### 3.2.1 Phosphorus

The average FWMCs of TP and DRP in runoff over the three rainfall events increased significantly ($p$<0.001) for all unamended waste applications when compared to the control soil. With the exception of DSW, TP concentrations were reduced ($p$<0.001) following application of PAC and alum amended (without zeolite addition) wastes, and DRP concentrations were reduced for dairy and pig wastes ($p$<0.001) and for DSW ($p$<0.01) (Figure 1, Table 3). Further reductions in TP were measured for dairy and pig wastes ($p$<0.001) amended with combined zeolite and PAC/alum, however DRP concentrations were not significantly different.

### 3.2.2 Nitrogen

The FWMC for TN from the control soil ranged from 8.5 (RE1) to 11 mg $L^{-1}$ (RE3). The TN concentrations in runoff were observed to increase for all unamended slurry applications compared to the control soil ($p$<0.001). Ammonium-N concentrations were highest for pig slurry, followed by dairy slurry and DSW, while TON concentrations in runoff, primarily as $NO_3$-N, were highest for dairy slurry, followed by pig slurry and DSW (Table 3). The FWMC of TN, $NH_4$-N and $NO_3$-N in runoff for chemically amended wastes (without zeolite addition) over the three rainfall events were reduced by 40%, 57% and 45% (dairy slurry), 13%, 0% and 0% (pig slurry), and 8%, 32% and 26% (DSW) compared to unamended wastes. Application of combined zeolite and chemical amendments further reduced TN, $NH_4$-N and $NO_3$-N concentrations in runoff from all three wastes over the three rainfall events to below those achieved by chemical amendments only (Figure 2). Decreases in TN of amended wastes compared to unamended wastes were significant for all treatments, except for alum-amended DSW and PAC amended pig slurry ($p<0.001$). The TN concentrations in runoff using dual zeolite and PAC/alum amendments were less than those using PAC/alum amendments only for all wastes ($p<0.001$). The combined amendments reduced $NO_3$-N concentrations in runoff below those of unamended wastes by 49% for dairy slurry (325 to 167 μg $L^{-1}$), 31% for pig slurry (168 to 115 μg $L^{-1}$), and 38% for DSW (42 to 26 μg $L^{-1}$).

### 3.2.3 Suspended solids

The average FWMC of SS from the control soil (27 mg $L^{-1}$) for all three rainfall events increased significantly ($p<0.001$) following application of unamended wastes (Figure 3). The average FWMC of SS from wastes amended with PAC and alum reduced by 63% (dairy slurry), 49% (pig slurry) and 57% (DSW) compared to unamended controls. These removals did not change significantly for dairy and pig slurries (73% and 44%) using dual zeolite and chemical amendments, and resulted in higher SS concentrations for DSW amended with dual zeolite and alum (85 mg $L^{-1}$) than with alum only (48 mg $L^{-1}$).

The average FWMC of PP in runoff was highly correlated with corresponding SS concentrations for dairy slurry ($R^2 = 0.92$) and to a lesser extent for pig slurry ($R^2 = 0.64$) and DSW ($R^2 = 0.50$) (Figure 4).

### 3.2.4 pH

Over the three rainfall events, the average pH in runoff from PAC-amended dairy slurry was lower than unamended dairy slurry (Table 3). There was no significant difference in pH between unamended and PAC-amended pig slurry and unamended and alum-amended DSW (Table 3). The average pH in runoff over the three rainfall events from dairy and pig slurries amended with zeolite and PAC was lower than that for unamended slurries, but was higher in runoff from DSW amended with zeolite and alum.

## 4. Discussion

The amendments used in this study had specific removal capacities, predominantly zeolite for N removal and PAC/alum for P and SS removal. The combinations used were those that produced the best reductions of $NH_4$-N and WEP from the wastes (Section 2.4). The use of packed soil boxes and simulated rainfall is recognized as a practical, if limited, method to assess P transport from grassed and bare soils (Sharpley and Kleinman, 2003; Kleinman et al., 2004).

### 4.1 Phosphorus in runoff

Observed reductions in P using only PAC/alum amendments (without zeolite) were generally consistent with previous studies (Smith et al., 2001b; Elliott et al., 2005; O'Rourke et al., 2012). The average concentrations of TP in runoff following application of unamended dairy slurry increased from 0.87 mg $L^{-1}$ for the control soil to 8.7 mg $L^{-1}$. This is consistent with the findings of Preedy et al. (2001), who recorded peak TP concentrations of 7 mg $L^{-1}$ from dairy slurry (6% DM) exposed to 28 days of intermittent rainfall ranging in intensity from 0.2 – 3 mm $h^{-1}$ rainfall in a lysimeter plot study. The reduced runoff concentrations in TP and DRP for dairy slurry using PAC at a ratio of 1.25:1 Al:TP (87% and 70%, respectively) were similar to those reported by Hanrahan et al. (2009) (89% and 65%, respectively) at a time interval of 5 d between application of dairy waste and a simulated rainfall event. In the current study, reductions in TP for dairy slurry are dominated by reductions in PP (6.44 to 0.77 mg $L^{-1}$), and the average FWMC of PP and SS in runoff were related to one another (Figure 4). The comparatively high DM content of dairy slurry compared to the other wastes (Table 1) meant that, when applied to the soil, much of it remained on the surface for the duration of the experiment. This contrasted with the pig slurry and DSW, which infiltrated the soil quite quickly after application because of their lower DM contents. The position of the dairy slurry on the soil facilitated a higher direct exposure to rainfall compared to the other applied wastes, and resulted in higher runoff SS (Figure 3) and PP concentrations (Figure 1). Eroded P-enriched particles can be mobilized by rain splash detachment, flow detachment or dispersion (Miller et al., 2009), and may be transported significant distances (Sharpley et al., 1999). Our results indicate that suspended dairy slurry solids, as opposed to soil solids, may be the principal transport mechanism for runoff P, predominantly as PP, from unamended slurry. The addition of PAC and PAC/zeolite to the dairy slurry reduced SS and PP concentrations. It is likely that release of $Al^{3+}$ flocculants from the PAC reduced the extent of fragmentation of the slurry into primary particles, hence reducing the concentration of SS transported by overland flow. The ratio of PP:TP reduced from 0.74 for unamended slurry to 0.36 for PAC amended slurry and 0.25 for combined zeolite and PAC amended dairy slurry, confirming that PAC, and not zeolite, is the most effective of the two amendments  in binding PP.

The SS concentrations in runoff from unamended pig slurry were much lower than those of unamended dairy slurry, as were the TP concentrations. The correlation between PP and SS for pig slurry was not as strong as for dairy slurry (Figure 4). This was likely due to the lower DM content of the pig slurry (Table 1). As a consequence, it is likely that the same opportunity for particle segregation from the slurry was not available and thus PP in runoff was not as prevalent as for dairy slurry (PP:TP = 0.32). The addition of PAC amendment only (no zeolite) increased the PP:TP ratio to 0.53, while the ratio for dual zeolite and PAC was similar (0.49). The overall DRP removal rates for pig slurry were similar to those of previous studies. In a runoff experiment to evaluate the impact of alum and aluminum chloride on swine manure applied to small grassed plots, Smith et al. (2001b) observed DRP reductions of 4.6 mg $L^{-1}$ in runoff between unamended manure and manure treated with 1:1 Al:TP molar ratio. This represented an 84% reduction in DRP, and is comparable to the 77% reduction measured in the current study using PAC at the same ratio. The removal rates in the current study increased to 92% when combined zeolite and PAC amendments were applied.

Very few data exist on runoff P concentrations from DSW applied to grassed soil under simulated rainfall conditions. In a study to measure the effects of rainfall events on P and SS losses from a grassed soil, Serrenho et al. (2012) reported an approximate TP reduction of 80% from relatively dilute DSW (DM = 0.2%, TP = 14.2 mg $L^{-1}$) amended with alum at a stoichiometric ratio of 8.8:1. They reported a weak correlation ($R^2 = 0.15$) between PP and SS in runoff for the unamended DSW, but a high PP:TP ratio of 0.75. In the current study, a lower stoichiometric ratio (5:1) of alum amendment resulted in a lower TP reduction of 15% for a stronger DSW than that of Serrenho et al. (2012) (Table 1). It is likely that application of the higher alum ratio by Serrenho et al. (2012) was more successful in sorbing dissolved P to the soil than in the current study and P-enriched soil particles were then mobilized in runoff. In the current study, both alum and dual zeolite and alum amendments resulted in similar reductions in PP (43% and 48%, respectively) compared to unamended DSW. Use of alum only (no zeolite) did not reduce dissolved P below that of unamended waste. In contrast, dual application of zeolite and alum reduced both DRP and DUP by 53%, indicating that zeolite may have contributed to dissolved P removal in runoff from DSW. The PP:TP ratios for the unamended DSW, alum amended DSW and dual zeolite and alum amended DSW were 0.56, 0.38 and 0.59, respectively. These, combined with the weak correlation between PP and SS in runoff (Figure 4), suggest that dissolved P losses may be just as significant as PP losses for the rates of amendments used.

## 4.2 Nitrogen in runoff

The results of this study confirm the results of previous studies using specific amendments in the treatment of agricultural wastes for N (Nguyen and Tanner, 1998; Widiastuti et al., 2011). The observed reductions in runoff $NH_4$-N compared to unamended wastes were highest for pig slurry, followed by dairy slurry and DSW (Table 3). The reduction in $NH_4$-N in runoff from dairy slurry amended with PAC (57%) compared to unamended dairy slurry was consistent with the findings of Brennan et al., (2012) (62%). Application of combined zeolite and PAC/alum amendments reduced $NH_4$-N concentrations in runoff to approximately those of the control soil (3.37 mg $L^{-1}$) for dairy slurry (5.25 mg $L^{-1}$) and DSW (3.37 mg $L^{-1}$), but not for pig slurry (13.95 mg $L^{-1}$).

The physical composition of the three wastes (Table 1) and their appearance on the grassed soil was quite different. While dairy slurry remained on top of the grassed soil, both the pig slurry and DSW infiltrated it more easily. Torbert et al. (2005)

observed that the interaction between the applied manure and runoff water is of primary importance for the loss of pollutants. A high interaction between the grass thatch layer and the manure will greatly reduce the amount of manure that leaves the grassed soil as particles, but also increases the interaction that the runoff water has with the surface area of the manure. Although grass was cropped to approx. 25mm in this study, it is likely that the zeolite benefited from more contact time with the dairy slurry than with either the pig slurry or DSW, and this may have resulted in the lower $NH_4$-N in runoff for the dairy slurry. Conversely, the interaction time between the zeolite and pig slurry may have been insufficient to achieve a similar level of $NH_4$-N removal as measured for dairy slurry. We are not sure why the $NH_4$-N runoff removal rate for DSW was so high, but it may be possible that the alum may have sequestered some ammonia, or that pockets of DSW may have pooled on parts of the saturated soil surface, thereby facilitating a higher contact time with the zeolite. The $NH_4$-N concentrations for both pig and dairy slurries were 1800 mg $L^{-1}$, while that of the DSW was much lower at 164 mg $L^{-1}$, and this also may have influenced concentrations of $NH_4$-N in runoff.

Loss of $NH_4$-N from land applied wastes is of interest because such losses greatly reduce the fertilizer values of slurry (Misselbrook et al., 2002). More than 50% of applied N can be lost by ammonia volatization, with close to 50% of these emissions occurring in the first 24 h during and after slurry application (Sommer and Hutchings, 2001; Sommer et al., 2003). In an experiment to assess the effects of alum or zeolite addition to dairy slurry on ammonia volatization, Lefourt and Meisinger (2001) found that 65% of ammonia emissions in unamended slurry occurred within 24 h of exposure. Addition of alum at rates of 2.5% and 6.25% reduced these losses by 58%

and 57%, respectively, compared to unamended controls, with most of the losses occurring in the initial 12 h and negligible losses thereafter. In the same experiment, addition of zeolite, also at rates of 2.5% and 6.25%, reduced ammonia emissions by 22% and 47%, respectively, compared to the unamended controls, with most of the losses occurring in the initial 24 h period and at a reduced rate thereafter. While the modes of ammonia capture were different for both types of amendments (acidification for alum (Bussink et al., 1994) and availability of $NH_4$-N exchange sites for zeolite), ammoniacal capture occurred mostly within a 24 h period for both amendments, albeit at a much slower rate for zeolite. In the current study, the zeolite and chemical amendments were added immediately before application of the wastewaters to the flumes and it is likely that some ammonia may have volatilized in the initial 48 h period before the rainfall simulation took place. It may be beneficial, therefore, on a practical basis to add the zeolite to the wastewaters at least 24 h and chemicals at least 12 h prior to landspreading to facilitate reduced ammonia volatilization.

### 4.3 SS in runoff

Suspended sediment in runoff from the control soil was 0.99 kg ha$^{-1}$ and the largest increases following application of unamended wastes were for dairy slurry (19.5 kg ha$^{-1}$) followed by DSW (4.7 kg ha$^{-1}$) and pig slurry (4.0 kg ha$^{-1}$). The large increase for dairy slurry is consistent with its relatively high DM content compared to the other wastes (Table 1) and all SS fluxes were likely to have been influenced by the wet antecedent soil conditions. Reductions in runoff SS were highest when all three wastes were amended with PAC/alum only (no zeolite) (Table 3). These removal rates did not change significantly for both dairy and pig slurries when amended with dual zeolite and PAC, but reduced for DSW when amended with dual zeolite and alum.

This suggests that SS reduction is predominantly due to release of flocculants from the PAC/alum which aids adhesion of the SS in the wastes and in the soil thereby decreasing their susceptibility to loss in runoff. We are not sure why there was an increase in SS concentrations for the DSW when amended with dual zeolite and alum and it is interesting to note that there was no corresponding increase in PP or any of the other P fractions (Table 3). One possible explanation for this is that the increased SS release might have been mainly in the form of sand released from the soil (the soil comprised 57% sand) with corresponding lower P adsorption capacity than either the silt or clay fractions (Hansen et al., 2002).

### 4.4 Cost analysis of amendments

A preliminary cost analysis on use of dual zeolite and PAC/alum amendments indicates that high costs, particularly the cost of zeolite, may be a prohibitive factor in their widespread application. Taking the cost of amendments only (without ancillary costs of storage, application, mixing and spreading) at €1,150 tonne$^{-1}$ for zeolite (in Ireland), €480 tonne$^{-1}$ for PAC and €250 tonne$^{-1}$ for alum, the costs per m$^3$ of applied slurry based on application rates used in this study is €190 for dairy slurry, €188 for pig slurry and €84 for DSW. These compare with estimated costs per m$^3$ of €6.40 for dairy slurry, €5.60 for pig slurry and €0.80 for DSW using PAC/alum amendments only (Brennan et al., 2011). Therefore, the additional cost of using dual zeolite and chemical amendments is significantly higher than use of chemical only (by an order of magnitude in excess of 2 in the case of DSW) and consequently may not be an attractive mitigation option in areas where zeolite is not an indigenous natural material and where purchase costs may be prohibitive. Acknowledging that final costs may vary with location and availability of zeolite, it is nevertheless unlikely that widespread use of dual zeolite and chemical amendments in agricultural wastewaters will be economically sustainable in the short to medium term, and would be better suited to critical source areas (areas where there is a high risk of incidental losses in overland flow), or where land availability for spreading agricultural wastes is limited.

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**Table 1** Waste characterization for total phosphorus (TP), dissolved reactive phosphorus (DRP), total nitrogen (TN), ammonium ($NH_4$-N), pH and dry matter (DM) (n=3). The characterizations were carried out over the full experimental period of the study.

| Waste Type | TP | DRP | TN | $NH_4$-N | pH | DM |
|---|---|---|---|---|---|---|
| | ------------------------------------ | ---------- mg $L^{-1}$ ---------- | | ------------------------------------ | | % |
| Dairy slurry | 563±55 | 18±4 | 4174±554 | 1800±16 | 7.78±0.03 | 8.0±0.1 |
| Pig slurry | 619±30 | 42±1 | 2648±242 | 1814±87 | 7.49±0.05 | 2.6±0.1 |
| Dairy soiled water | 52±11 | 17.±1 | 748±76 | 163.7±3.0 | 6.89±0.01 | 0.7±0.3 |

**Table 2** Chemical composition of natural zeolite used. The zeolite was sieved to a particle size of 2.36-3.35 mm. All values expressed as percentages.

| $Al_2O_3$ | BaO | $Fe_2O_3$ | MnO | $SiO_2$ | CaO | MgO | $K_2O$ | Na2O | $TiO_2$ | $P_2O_5$ | SrO | Loss in ignition at 1000 °C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10.4 | 0.03 | 0.90 | 0.01 | 66.7 | 1.57 | 0.52 | 4.73 | 0.86 | 0.06 | <0.001 | 0.04 | 14.1 |

**Table 3** Flow weighted mean concentrations in runoff averaged over three rainfall events and % reductions (% R) from unamended slurries for total phosphorus (TP), particulate phosphorus (PP), total dissolved phosphorus (TDP), dissolved reactive phosphorus (DRP), dissolved unreactive phosphorus (DUP), total nitrogen (TN), ammonium ($NH_4$-N), nitrite ($NO_2$-N), nitrate ($NO_3$-N), suspended solids (SS) and pH, and % reduction or increase from unamended waste pH in runoff.

| **Waste application** | **TP (mg $L^{-1}$)** | **% R** | **PP (mg $L^{-1}$)** | **% R** | **TDP (mg $L^{-1}$)** | **% R** | **DRP (mg $L^{-1}$)** | **% R** | **DUP (mg $L^{-1}$)** | **% R** | **TN (mg $L^{-1}$)** | **% R** | **$NH_4$-N (mg $L^{-1}$)** | **% R** | **$NO_2$-N (µg $L^{-1}$)** | **% R** | **$NO_3$-N (µg $L^{-1}$)** | **% R** | **SS (mg $L^{-1}$)** | **% R** | **pH** | **% reduction (-) / increase (+) from unamended slurry pH in runoff** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Control soil** | 0.87 | - | 0.43 | - | 0.44 | - | 0.19 | - | 0.25 | - | 9.64 | - | 3.37 | - | 9 | - | 36 | - | 27 | - | 6.43 | - |
| **D(U)** | 8.68 | - | 6.44 | - | 2.23 | - | 1.16 | - | 1.07 | - | 41.00 | - | 16.53 | - | 380 | - | 325 | - | 535 | - | 6.73 | - |
| **D(CA)** | 2.14 | 75 | 0.77 | 88 | 1.37 | 39 | 0.60 | 48 | 0.77 | 28 | 25.54 | 40 | 7.11 | 57 | 179 | 53 | 180 | 45 | 198 | 63 | 6.30 | -6.4 |
| **D(A)** | 1.11 | 87 | 0.28 | 96 | 0.83 | 63 | 0.35 | 70 | 0.48 | 55 | 18.08 | 56 | 5.25 | 68 | 131 | 66 | 167 | 49 | 143 | 73 | 6.37 | -5.4 |
| **P(U)** | 5.28 | - | 1.69 | - | 3.59 | - | 2.60 | - | 0.99 | - | 41.02 | - | 26.10 | - | 42 | - | 168 | - | 101 | - | 6.58 | - |
| **P(CA)** | 2.00 | 62 | 1.06 | 38 | 0.95 | 74 | 0.60 | 77 | 0.35 | 65 | 35.56 | 13 | 26.65 | - | 62 | - | 175 | - | 52 | 49 | 6.67 | 1.3 |
| **P(A)** | 1.00 | 81 | 0.49 | 71 | 0.51 | 86 | 0.22 | 92 | 0.29 | 70 | 22.48 | 45 | 13.95 | 47 | 42 | 1 | 115 | 31 | 57 | 44 | 6.21 | -5.6 |
| **DSW(U)** | 1.84 | - | 1.03 | - | 0.81 | - | 0.35 | - | 0.46 | - | 25.95 | - | 12.43 | - | 11 | - | 42 | - | 112 | - | 6.08 | - |
| **DSW(CA)** | 1.57 | 15 | 0.59 | 43 | 0.98 | - | 0.49 | - | 0.49 | - | 23.98 | 8 | 8.46 | 32 | 13 | - | 31 | 26 | 48 | 57 | 5.93 | -2.5 |
| **DSW (A)** | 0.92 | 50 | 0.54 | 48 | 0.38 | 53 | 0.17 | 53 | 0.21 | 54 | 14.33 | 45 | 3.37 | 73 | 14 | - | 26 | 38 | 85 | 25 | 6.95 | 14.3 |

| | |
|---|---|
| % R | % Reduction |
| D(U) | Unamended dairy slurry |
| D(CA) | Dairy slurry amended with PAC at 1.25:1 Al:TP (704 mg $L^{-1}$) |
| D(A) | Dairy slurry amended with zeolite at 2 g $g^{-1}$ DM (160 kg $m^{-3}$) and PAC at 1.25:1 Al:TP (704 mg $L^{-1}$) |
| P(U) | Unamended pig slurry |
| P(CA) | Pig slurry amended with PAC at 1:1 Al:TP (619 mg $L^{-1}$) |
| P(A) | Pig slurry amended with zeolite at 6 g $g^{-1}$ DM (156 kg $m^{-3}$) and PAC at 1:1 Al:TP (619 mg $L^{-1}$) |
| DSW(U) | Unamended dairy soiled water |
| DSW(CA) | Dairy soiled water amended with alum at 5:1 Al:TP (260 mg $L^{-1}$) |
| DSW(A) | Dairy soiled water amended with zeolite at 10 g $g^{-1}$ DM (70 kg $m^{-3}$) and alum at 5:1 Al:TP (260 mg $L^{-1}$) |

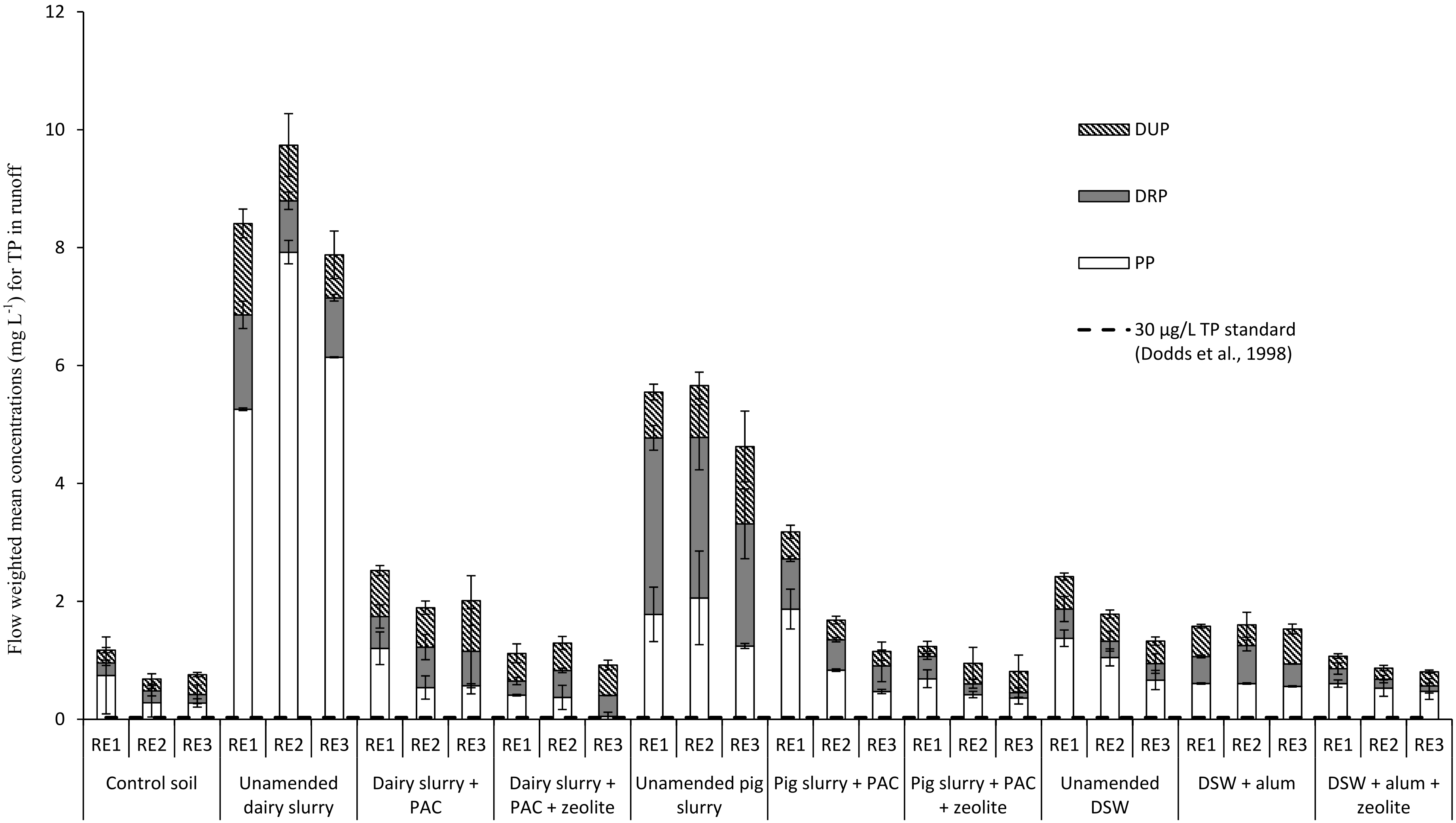

**Figure 1:** Histogram of flow weighted mean concentrations for total phosphorus (TP) comprising particluate phosphrus (PP), dissolved reactive phosphrus (DRP) and dissolved unreactive phosphrus (DUP) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h.

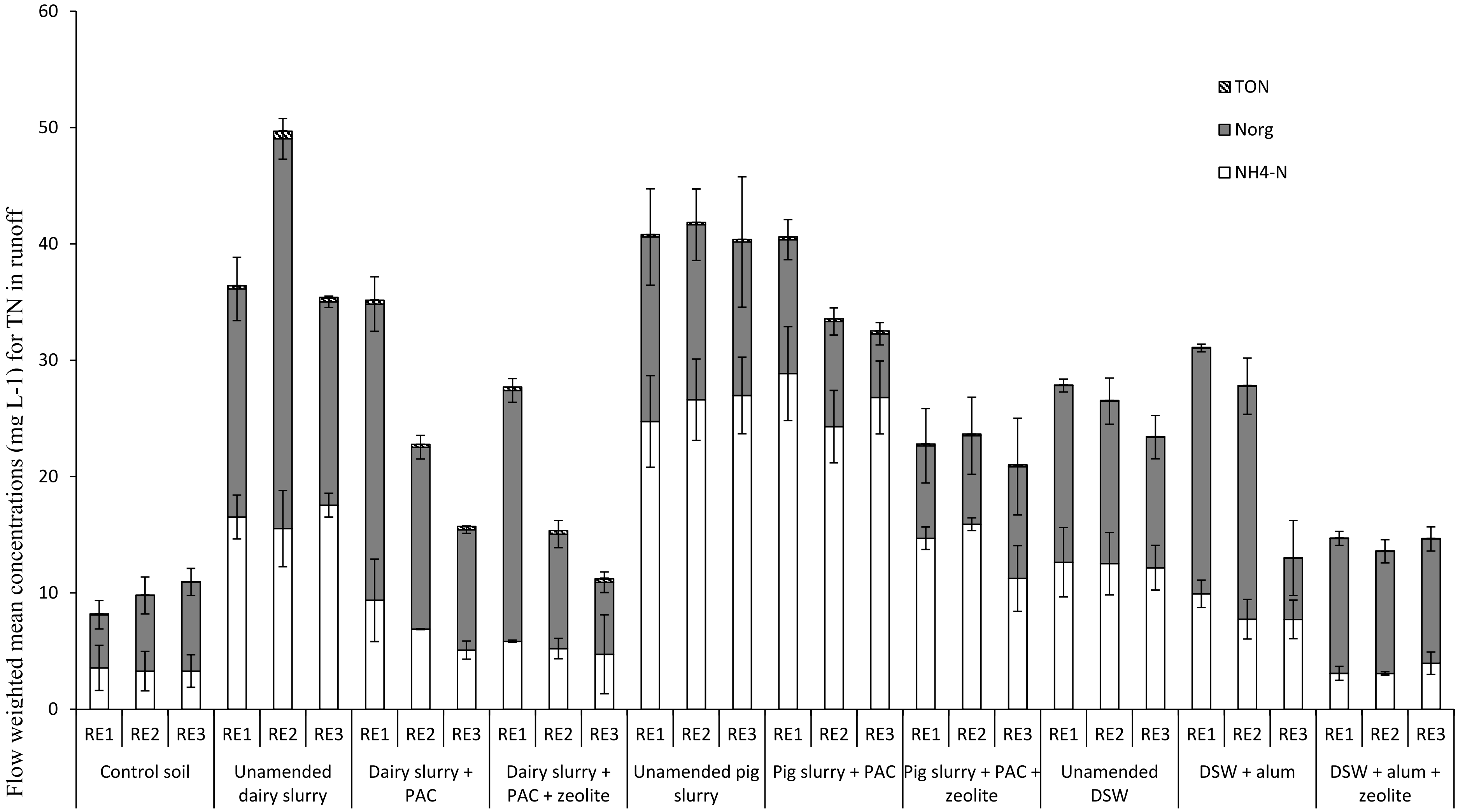

**Figure 2:** Histogram of flow weighted mean concentrations for total nitrogen (TN) comprising ammonium-N (NH4-N), organic N (Norg) and total oxidized nitrogen (TON) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h.

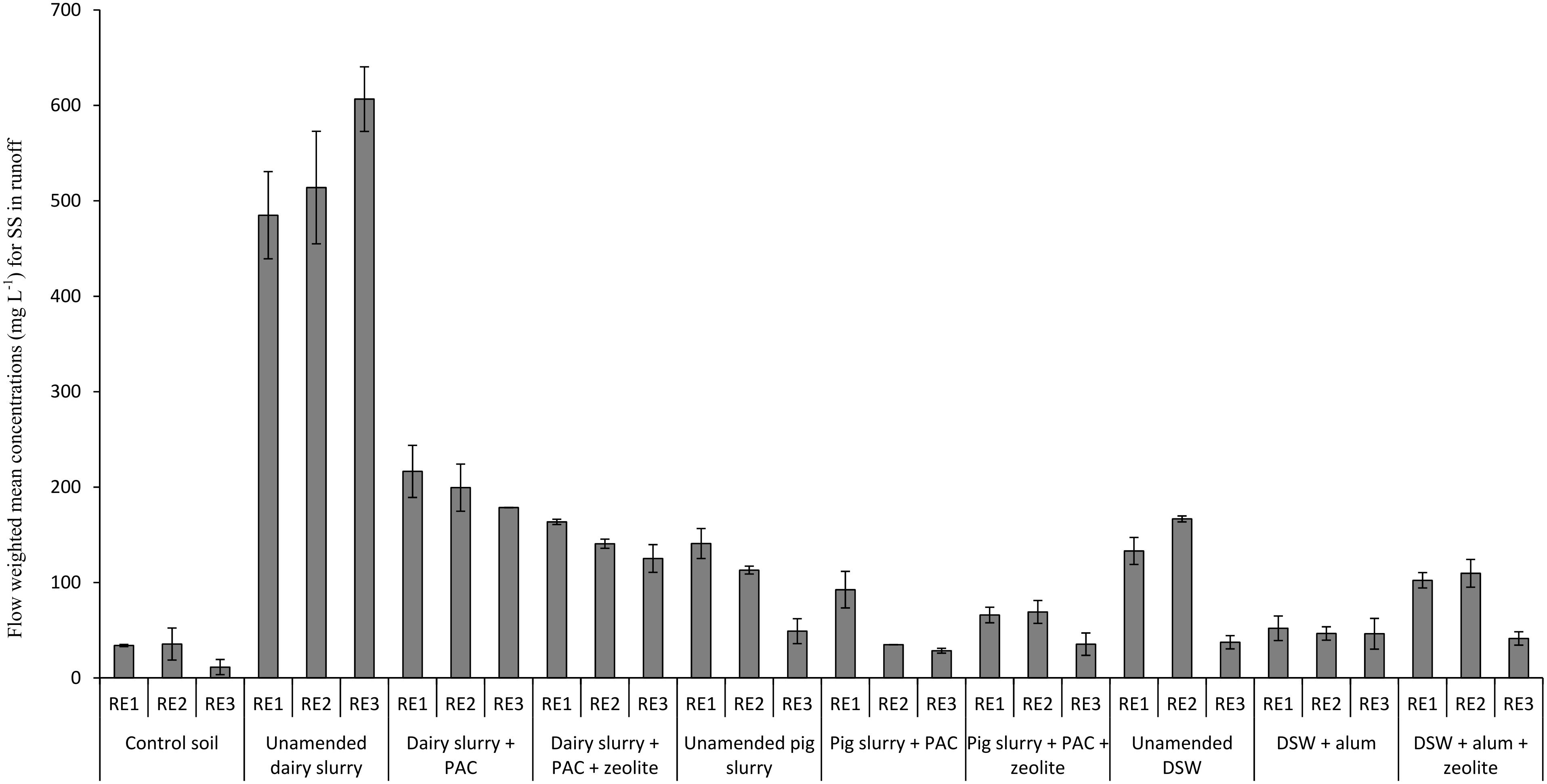

**Figure 3:** Histogram of flow weighted mean concentrations for SS in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h.

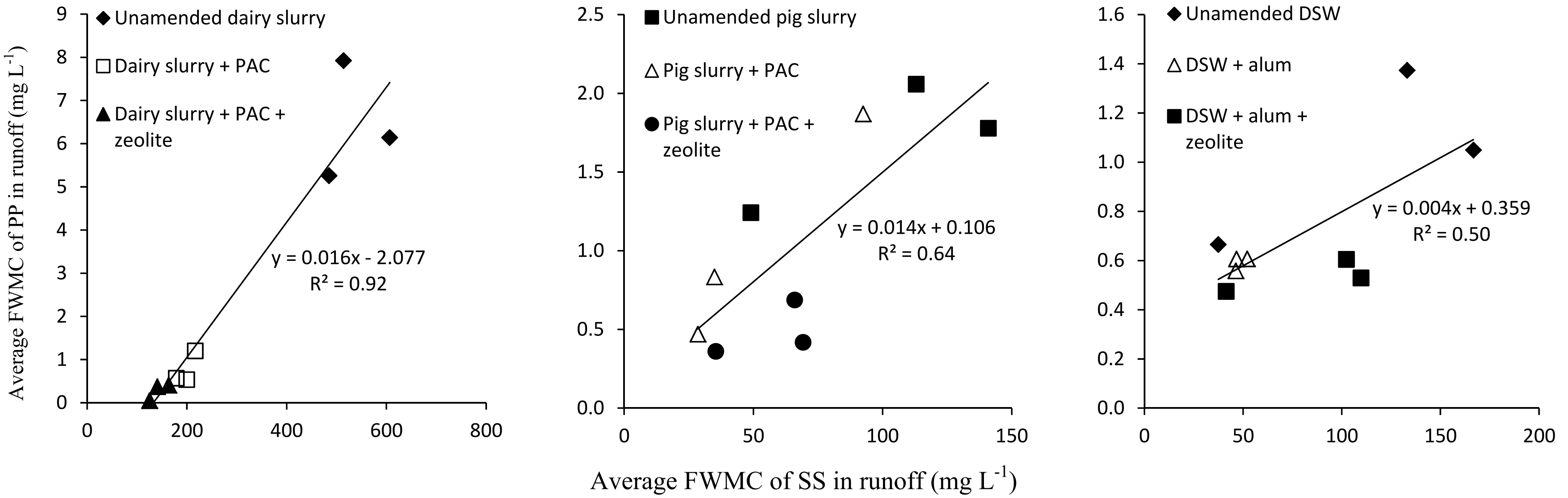

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**Figure 4:** Correlation between suspended solid (SS) concentrations and corresponding particulate phosphorus (PP) concentrations for dairy slurry, pig slurry and DSW averaged over all three rainfall events. The data includes unamended wastes, wastes amended with PAC/alum only (no zeolite) and combined zeolite and PAC/alum amendments. Lines represent a least squares regression analysis, with correlation coefficients ($R^2$) indicated.