

# Use of Zeolite with Alum and Polyaluminum Chloride Amendments to Mitigate Runoff Losses of Phosphorus, Nitrogen, and Suspended Solids from Agricultural Wastes Applied to Grassed Soils

J. G. Murnane, R. B. Brennan, M. G. Healy,\* and O. Fenton

## 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 polyaluminum chloride (PAC) with dairy and pig slurries or zeolite and alum with DSW. Four treatments were investigated in rainfall simulation studies: (i) control soil, (ii) agricultural wastes, (iii) dairy and pig slurries amended with PAC and DSW amended with alum, and (iv) dairy and pig slurries amended with zeolite and PAC and DSW amended with zeolite and alum. Our data showed that combined amendments of zeolite and PAC applied to dairy and pig slurries reduced total P (TP) in runoff by 87 and 81%, respectively, compared with unamended slurries. A combined amendment of zeolite and alum applied to DSW reduced TP in runoff by 50% compared with unamended DSW. The corresponding reductions in total N (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 with unamended controls, but these results 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 the 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.

## Core Ideas

- Surface runoff studies have mainly focused on mitigation of one contaminant.
- This paper optimizes mitigation of two contaminants by optimizing amendments.
- Zeolite and chemical mixtures increased N and P removal from agricultural waste.
- More N and P were removed from zeolite and chemical mixtures than chemicals only.
- Zeolite and chemical mixtures improved suspended solids removal from dairy soiled water runoff.

**E**XCESSIVE APPLICATION of agricultural waste to soils may have environmental impacts, including phosphorus (P), nitrogen (N), and suspended solids (SS) losses and increased 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-term and long-term effects of agricultural waste application to the soil structure (McDowell et al., 2004). Event P losses in surface runoff after land application of agricultural wastes may be dominated by particulate P (PP) (Preedy et al., 2001) or by dissolved P, 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), whereas 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 ( $\text{NH}_4\text{-N}$ ) (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 after land application has been shown to be effective (Smith et al., 2001b; Kalbasi and Karthikeyan, 2004; Moore

Copyright © 2015 American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. 5585 Guilford Rd., Madison, WI 53711 USA. All rights reserved.

J. Environ. Qual. 44:1674–1683 (2015)

doi:10.2134/jeq2014.07.0319

Received 29 July 2014.

Accepted 8 June 2015.

\*Corresponding author (mark.healy@nuigalway.ie).

J.G. Murnane, R.B. Brennan, and M.G. Healy, Civil Engineering, National Univ. of Ireland, Galway, Co. Galway, Rep. of Ireland; J.G. Murnane, Civil Engineering and Materials Science, Univ. of Limerick, Co. Limerick, Rep. of Ireland; O. Fenton, Teagasc, Johnstown Castle, Environment Research Centre, Co. Wexford, Rep. of Ireland. Assigned to Associate Editor Mark Reiter.

**Abbreviations:** DM, dry matter; DRP, dissolved reactive phosphorus; DSW, dairy-soiled water; FWMC, flow-weighted mean concentration; PAC, polyaluminum chloride; PP, particulate phosphorus; RCF, relative centrifugal force; SS, suspended solids; TDP, total dissolved phosphorus; TN, total nitrogen; TON, total oxidized nitrogen; WEP, water-extractable phosphorus.

and Edwards, 2007). In contrast to most studies, Brennan et al. (2012) tested the effect of polyaluminum chloride (PAC) [ $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$ ; 10%  $\text{Al}_2\text{O}_3$ ], alum [ $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ; 8%  $\text{Al}_2\text{O}_3$ ], or lime [ $\text{Ca}(\text{OH})_2$ ] on P and N losses. They found that the three chemicals did not have a significant effect on N losses after the first rainfall event 2 d 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 to 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  $\text{NH}_4\text{-N}$  from pig and dairy slurries was over 98% at a hydraulic loading rate (HLR) of  $0.47 \text{ mm min}^{-1}$  and 50 to 90% at a HLR of  $15.9 \text{ mm min}^{-1}$ . Zeolite has also been shown to be effective in reducing ammonia emissions from dairy slurry stored in the holding pit of a 100-cow freestall 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.

## Materials and Methods

### Chemical and Physical Analyses

#### Agricultural Wastes

Total P (TP) was measured using acid persulfate digestion and dissolved reactive P (DRP) by centrifuging at 17,970 relative centrifugal force (RCF) for 5 min, filtering through  $0.45\text{-}\mu\text{m}$  filters, and measuring colorimetrically using a nutrient analyzer (Konelab 20, Thermo Clinical Laboratories Systems). Total N was measured using a BioTector TOC TN TP Analyzer (BioTector Analytical Systems Ltd.). Ammonium was extracted from fresh waste by shaking 10 g of waste in 200 mL of  $0.1 \text{ mol L}^{-1}$  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), and dry matter (DM) was measured by drying at  $105^\circ\text{C}$  for 24 h. All parameters were tested in accordance with the standard methods (APHA, 2005).

#### Zeolite

The zeolite was sieved to a particle size of 2.36 to 3.35 mm and analyzed for  $\text{Al}_2\text{O}_3$ , BaO,  $\text{Fe}_2\text{O}_3$ , MnO,  $\text{TiO}_2$ , and SrO using inductively coupled plasma mass spectrometry; CaO, MgO,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$  using atomic adsorption spectrometry;  $\text{P}_2\text{O}_5$  by colorimetry; and  $\text{SiO}_2$  by fusion (Vogel, 1989).

#### Soil

Soil P was measured by air drying soil cores ( $n = 3$ ) at  $40^\circ\text{C}$  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 BS1377-2 (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 P (WEP) was measured by shaking 1 g of fresh soil in 100 mL of deionized water for 30 min, filtering the supernatant water through  $0.45\text{-}\mu\text{m}$  filter paper, and measuring the P colorimetrically.

#### 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,  $1.2 \mu\text{m}$ ) filter paper (APHA, 2005). Subsamples were filtered through  $0.45\text{-}\mu\text{m}$  filters and measured colorimetrically for DRP,  $\text{NH}_4\text{-N}$ , total oxidized N (TON), and nitrite-N ( $\text{NO}_2\text{-N}$ ) using a nutrient analyzer (Konelab 20, Thermo Clinical Labsystems). Unfiltered subsamples were tested for TP and total dissolved P (TDP) using acid persulfate digestion and for TN using a BioTector Analyzer (BioTector Analytical Systems Ltd.).

### Materials Collection and Characterization

#### Agricultural Wastes

Three types of agricultural wastes were collected from the Teagasc Research Centre, Moorepark, Fermoy, Co. Cork: (i) dairy slurry from a slatted unit housing dairy cows, (ii) pig slurry from an integrated pig unit, and (iii) 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, silage effluent, fertilizers and parlor washings, which have a DM content  $<1\%$  and a 5-d biochemical oxygen demand  $<2500 \text{ mg L}^{-1}$ . All wastes were homogenized immediately before 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  $11^\circ\text{C}$  for 12 h before the experimental onset. Triplicate samples of each waste were tested for TP, DRP, TN,  $\text{NH}_4\text{-N}$ , pH, and DM (Table 1).

**Table 1. Waste characterization for total P, dissolved reactive P, total N, ammonium, pH, and dry matter ( $n = 3$ ). The characterizations were carried out over the full experimental period of the study.**

Waste type	TP†	DRP	TN	$\text{NH}_4\text{-N}$	pH	DM
Dairy slurry	$563 \pm 55$	$18 \pm 4$	$4174 \pm 554$	$1800 \pm 16$	$7.78 \pm 0.03$	$8.0 \pm 0.1$
Pig slurry	$619 \pm 30$	$42 \pm 1$	$2648 \pm 242$	$1814 \pm 87$	$7.49 \pm 0.05$	$2.6 \pm 0.1$
Dairy-soiled water	$52 \pm 11$	$17 \pm 1$	$748 \pm 76$	$163.7 \pm 3.0$	$6.89 \pm 0.01$	$0.7 \pm 0.3$

† DM, dry matter; DRP, dissolved reactive P; total N, TN; TP, total P.

## 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<sub>2</sub>) and aluminum (10.4% Al<sub>2</sub>O<sub>3</sub>) (Table 2).

## Soil

Intact grassed soil samples (500 mm long, 300 mm wide, and 100 mm deep) were collected from grassland that 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<sup>-1</sup> (mg P L<sup>-1</sup>), a WEP of 2.3 ± 0.4 mg P kg<sup>-1</sup>, 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).

## Adsorption Capacity of Zeolite

The ability of zeolite to remove P (PO<sub>4</sub>-P) and N (NH<sub>4</sub>-N) from the three types of wastes was first investigated using a multipoint Langmuir isotherm (McBride, 2000):

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

where  $C_e$  is the concentration of P or N in solution at equilibrium (mg L<sup>-1</sup>),  $x/m$  is the mass of P or N adsorbed per unit mass of amendments (g kg<sup>-1</sup>) 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<sup>-1</sup>).

Zeolite was sieved ( $n = 3$ ) to a particle size of 2.36 to 3.35 mm, and 4 g were 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).

## 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<sub>4</sub>-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<sub>4</sub>-N by adding 25 mL of the supernatant to 500 mL of 0.1 mol L<sup>-1</sup> 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<sub>4</sub>-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<sub>4</sub>-N removal: (i) PAC, comprising 10% Al<sub>2</sub>O<sub>3</sub> to the dairy slurry at five Al:TP stoichiometric ratios between 0.5:1 and 1.5:1; (ii) PAC, comprising 10% Al<sub>2</sub>O<sub>3</sub> to the pig slurry at five Al:TP stoichiometric ratios between 0.3:1 and 1.25:1; and (iii) alum, comprising Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O 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<sub>4</sub>-N concentrations and WEP from the wastes was used in the runoff experiments.

## Rainfall Simulation Study

Runoff experiments were conducted in triplicate comparing (i) control soil, (ii) animal wastes, (iii) DSW amended with alum and dairy and pig slurries amended with PAC, and (iv) DSW amended with zeolite and alum and dairy and pig slurries amended with zeolite and PAC. Zeolite was applied at ratios of 2 g g<sup>-1</sup> DM to the dairy slurry, 6 g g<sup>-1</sup> DM to the pig slurry, and 10 g g<sup>-1</sup> DM to the DSW. Polyaluminum chloride 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<sup>-1</sup> for pig and dairy slurries and 50 m<sup>3</sup> ha<sup>-1</sup> for DSW, which equated to 31, 34, and 50 t ha<sup>-1</sup> 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.

## Runoff Boxes and Rainfall Simulation

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

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

Table 2. Chemical composition of natural zeolite used. The zeolite was sieved to a particle size of 2.36 to 3.35 mm.

Al <sub>2</sub> O <sub>3</sub>	BaO	Fe <sub>2</sub> O <sub>3</sub>	MnO	SiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	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

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 before testing. All experiments were performed within 14 d of soil core collection. Immediately before the start of each runoff box experiment, each core was trimmed to a typical length of between 450 and 500 mm and butted against an adjacent core to form a continuous surface of two or 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 or PAC/alum only were spread on the soil and left for 48 h. At  $t = 72, 96,$  and  $120$  h, successive rainfall events (RE1, RE2, and RE3), with an intensity of approximately  $10 \text{ mm h}^{-1}$ , 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 after each rainfall simulation.

## Runoff Analysis

Each of the samples taken at 5-min intervals was tested for pH and for SS. Subsamples, also taken at 5-min intervals, were measured for DRP,  $\text{NH}_4\text{-N}$ , TON, and  $\text{NO}_2\text{-N}$ . Nitrate-N was calculated by subtracting  $\text{NO}_2\text{-N}$  from TON. Unfiltered subsamples, taken at 10, 20, and 30 min after continuous runoff, were tested for TP, TDP, and TN. Dissolved unreactive P was calculated by subtracting DRP from TDP, and PP was calculated by subtracting TDP from TP.

## 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 postanalysis residuals for normality and homogeneity of variance.

## Results

### Adsorption Capacity and Bench-Scale Studies

The monolayer adsorption capacity of zeolite,  $q_{\text{max}}$ , ranged from 0.06 (pig slurry) to 0.31 (dairy slurry)  $\text{mg P g}^{-1}$  ( $\text{PO}_4\text{-P}$ ) and from 0.74 (DSW) to 7.88 (pig slurry)  $\text{mg N g}^{-1}$  ( $\text{NH}_4\text{-N}$ ). The optimum combined amendment application rates for reduction of  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  for dairy slurry were  $2 \text{ g g}^{-1}$  DM of zeolite with a stoichiometric PAC ratio of 1.25:1 (Al:TP). The corresponding rates for pig slurry were  $6 \text{ g g}^{-1}$  DM of zeolite with a stoichiometric PAC ratio of 1:1 (Al:TP) and for DSW were

$10 \text{ g g}^{-1}$  DM of zeolite with a stoichiometric alum ratio of 5:1 (Al:TP).

### Runoff from Laboratory Rainfall Simulation Study

#### 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 with the control soil. With the exception of DSW, TP concentrations were reduced ( $p < 0.001$ ) after 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 ( $p < 0.01$ ) (Fig. 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.

#### Nitrogen

The FWMCs for TN from the control soil ranged from 8.5 (RE1) to  $11 \text{ mg L}^{-1}$  (RE3). The TN concentrations in runoff were observed to increase for all unamended slurry applications compared with the control soil ( $p < 0.001$ ). Ammonium-N concentrations were highest for pig slurry, followed by dairy slurry and DSW, whereas TON concentrations in runoff, primarily as  $\text{NO}_3\text{-N}$ , were highest for dairy slurry, followed by pig slurry and DSW (Table 3). The FWMCs of TN,  $\text{NH}_4\text{-N}$ , and  $\text{NO}_3\text{-N}$  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 with unamended wastes. Application of combined zeolite and chemical amendments further reduced TN,  $\text{NH}_4\text{-N}$ , and  $\text{NO}_3\text{-N}$  concentrations in runoff from all three wastes over the three rainfall events to below those achieved by chemical amendments only (Fig. 2). Decreases in TN of amended wastes compared with 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 with 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  $\text{NO}_3\text{-N}$  concentrations in runoff below those of unamended wastes by 49% for dairy slurry ( $325\text{--}167 \text{ }\mu\text{g L}^{-1}$ ), 31% for pig slurry ( $168\text{--}115 \text{ }\mu\text{g L}^{-1}$ ), and 38% for DSW ( $42\text{--}26 \text{ }\mu\text{g L}^{-1}$ ).

#### Suspended Solids

The average FWMC of SS from the control soil ( $27 \text{ mg L}^{-1}$ ) for all three rainfall events increased significantly ( $p < 0.001$ ) after application of unamended wastes (Fig. 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 with unamended controls. These removal rates 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 ( $85 \text{ mg L}^{-1}$ ) than with alum only ( $48 \text{ mg L}^{-1}$ ).

The average FWMC of PP in runoff was highly correlated with corresponding SS concentrations for dairy slurry ( $R^2 =$

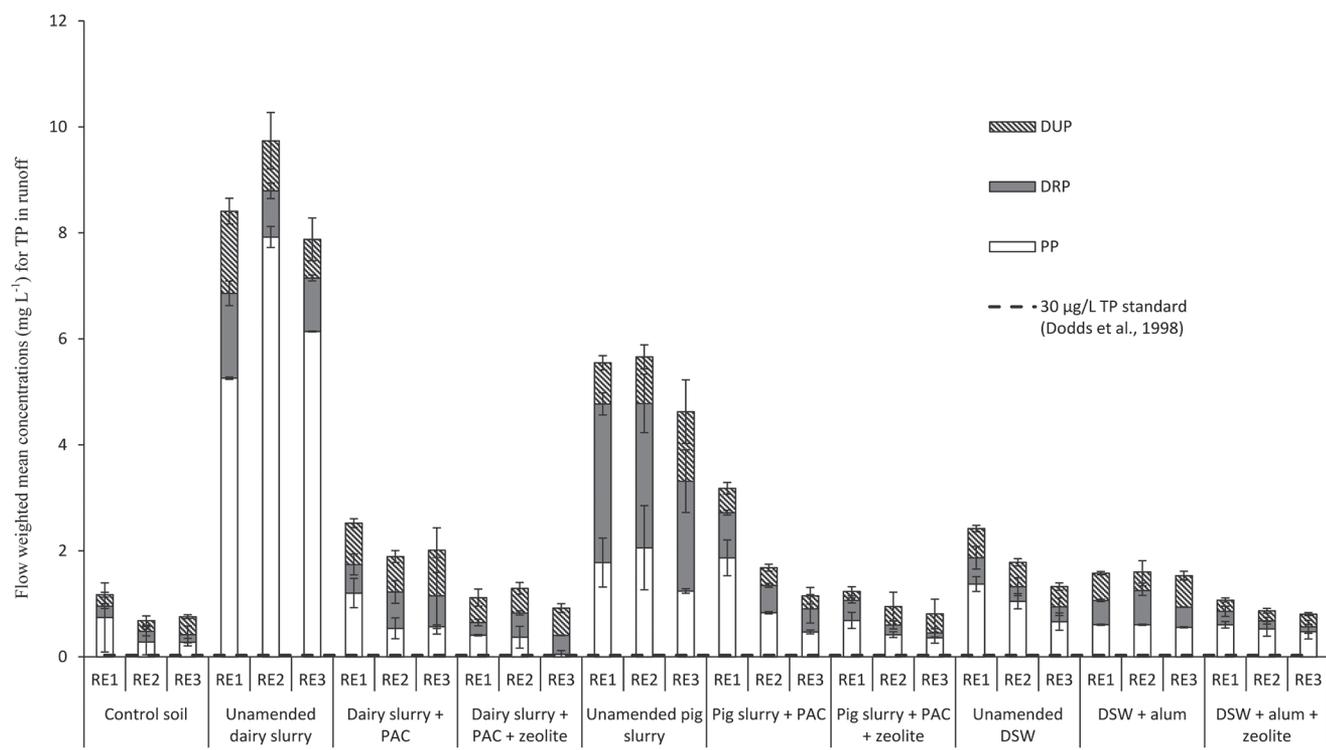


Fig. 1. Histogram of flow-weighted mean concentrations for total P (TP) comprising particulate P (PP), dissolved reactive P (DRP), and dissolved unreactive P (DUP) in runoff from rainfall event 1 (RE1) at  $t = 72$  h, rainfall event 2 (RE2) at  $t = 92$  h, and rainfall event 3 (RE3) at  $t = 120$  h. Data regarding TP standard are from Dodds et al. (1998). DSW, dairy-soiled water; PAC, polyaluminum chloride.

0.92) and to a lesser extent for pig slurry ( $R^2 = 0.64$ ) and DSW ( $R^2 = 0.50$ ) (Fig. 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

Table 3. Flow-weighted mean concentrations in runoff averaged over three rainfall events and percent reductions from unamended slurries for total P, particulate P, total dissolved P, dissolved reactive P, dissolved unreactive P, total N, ammonium, nitrite, nitrate, suspended solids, and pH and % reduction or increase from unamended waste pH in runoff.

Waste application†	TP‡	PP	TDP	DRP	DUP	TN	NH <sub>4</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N	SS	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

† D(A), dairy slurry amended with zeolite at  $2 \text{ g g}^{-1}$  dry matter (DM) ( $160 \text{ kg m}^{-3}$ ) and polyaluminum chloride (PAC) at 1.25:1 Al:total P (TP) ( $704 \text{ mg L}^{-1}$ ); D(CA), dairy slurry amended with PAC at 1.25:1 Al:TP ( $704 \text{ mg L}^{-1}$ ); DSW(A), dairy-soiled water amended with zeolite at  $10 \text{ g g}^{-1}$  DM ( $70 \text{ kg m}^{-3}$ ) and alum at 5:1 Al:TP ( $260 \text{ mg L}^{-1}$ ); DSW(CA), dairy-soiled water amended with alum at 5:1 Al:TP ( $260 \text{ mg L}^{-1}$ ); DSW(U), unamended dairy-soiled water; D(U), unamended dairy slurry; P(A), pig slurry amended with zeolite at  $6 \text{ g g}^{-1}$  DM ( $156 \text{ kg m}^{-3}$ ) and PAC at 1:1 Al:TP ( $619 \text{ mg L}^{-1}$ ); P(CA), pig slurry amended with PAC at 1:1 Al:TP ( $619 \text{ mg L}^{-1}$ ); P(U), unamended pig slurry.

‡ DRP, dissolved reactive P; DUP, dissolved unreactive P; PP, particulate P; SS, suspended solids; TDP, total dissolved P; TP, total P.

§ Values in parentheses are % reduction.

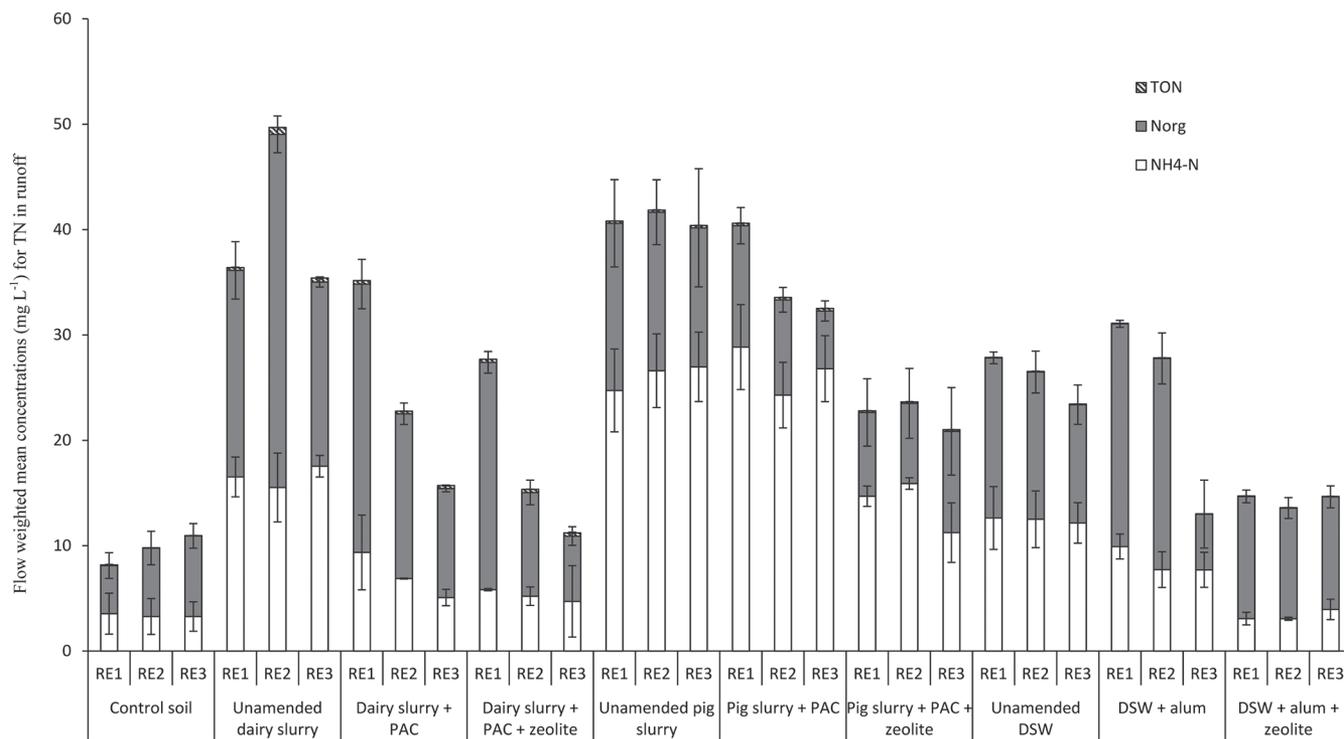


Fig. 2. Histogram of flow-weighted mean concentrations for total N (TN) comprising  $\text{NH}_4\text{-N}$ , organic N ( $\text{N}_{\text{org}}$ ), and total oxidized N (TON) in runoff from rainfall event 1 (RE1) at  $t = 72$  h, rainfall event 2 (RE2) at  $t = 92$  h, and rainfall event 3 (RE3) at  $t = 120$  h. DSW, dairy-soiled water; PAC, polyaluminum chloride.

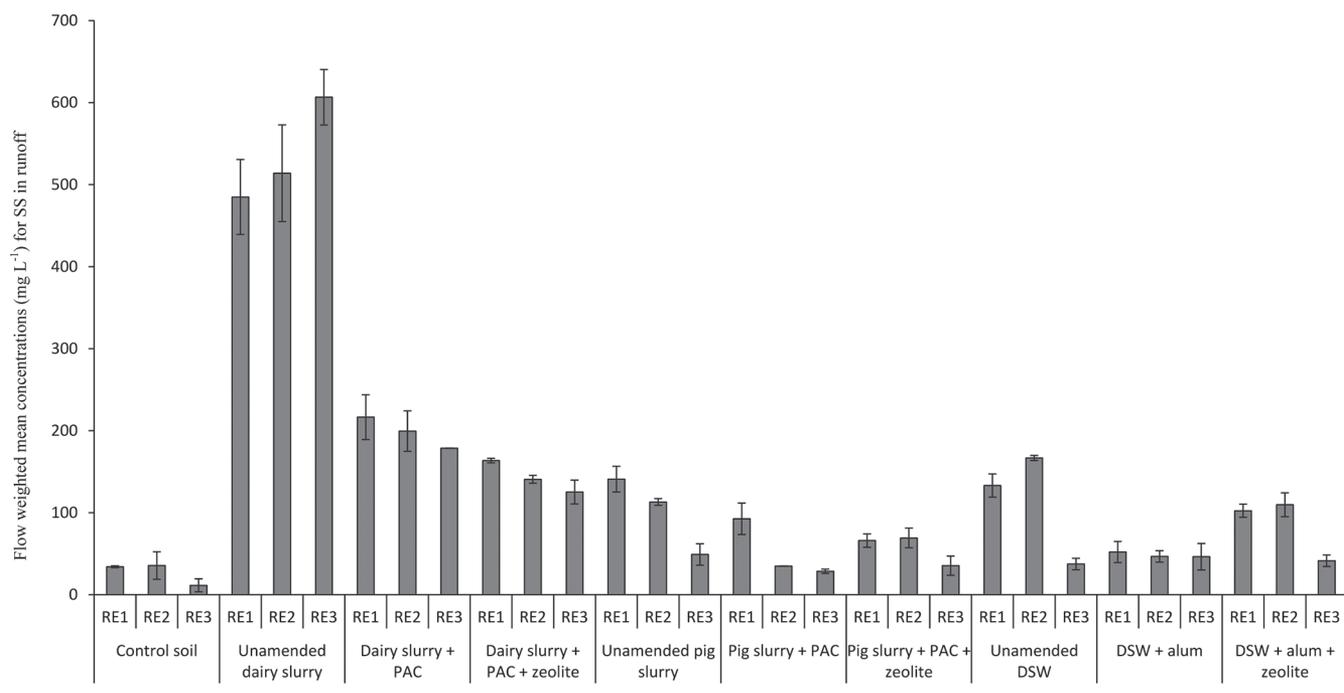


Fig. 3. Histogram of flow-weighted mean concentrations for suspended sediment (SS) in runoff from rainfall event 1 (RE1) at  $t = 72$  h, rainfall event 2 (RE2) at  $t = 92$  h, and rainfall event 3 (RE3) at  $t = 120$  h. DSW, dairy-soiled water; PAC, polyaluminum chloride.

for unamended slurries but was higher in runoff from DSW amended with zeolite and alum.

## 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  $\text{NH}_4\text{-N}$  and WEP from the wastes (optimum zeolite application). 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).

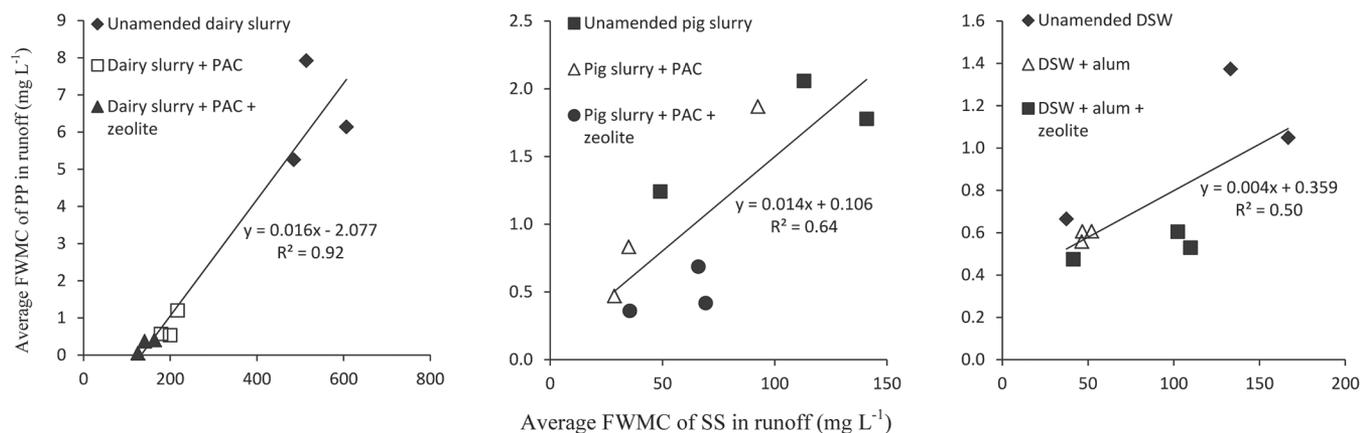


Fig. 4. Correlation between suspended solid (SS) concentrations and corresponding particulate P (PP) concentrations for dairy slurry, pig slurry, and dairy-soiled water (DSW) averaged over all three rainfall events. The data include unamended wastes, wastes amended with polyaluminum chloride (PAC)/alum only (no zeolite), and combined zeolite and PAC/alum amendments. Lines represent a least squares regression analysis, with  $R^2$  values indicated.

### 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 after application of unamended dairy slurry increased from 0.87 to 8.7 mg L<sup>-1</sup> for the control soil. This is consistent with the findings of Preedy et al. (2001), who recorded peak TP concentrations of 7 mg L<sup>-1</sup> from dairy slurry (6% DM) exposed to 28 d of intermittent rainfall ranging in intensity from 0.2 to 3 mm h<sup>-1</sup> 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 (6.44–0.77 mg L<sup>-1</sup>), and the average FWMCs of PP and SS in runoff were related to one another (Fig. 4). The comparatively high DM content of dairy slurry compared with 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 with the other applied wastes and resulted in higher runoff SS (Fig. 3) and PP concentrations (Fig. 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<sup>3+</sup> 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, 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 (Fig. 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, whereas 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<sup>-1</sup> 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 a TP reduction of approximately 80% from relatively dilute DSW (DM = 0.2%; TP = 14.2 mg L<sup>-1</sup>) 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 with 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 dissolved unreactive P 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 results, combined with the weak correlation between PP and SS in runoff (Fig. 4), suggest that dissolved P losses may be just as significant as PP losses for the rates of amendments used.

## 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  $\text{NH}_4\text{-N}$  compared with unamended wastes were highest for pig slurry, followed by dairy slurry and DSW (Table 3). The reduction in  $\text{NH}_4\text{-N}$  in runoff from dairy slurry amended with PAC (57%) compared with unamended dairy slurry was consistent with the findings of Brennan et al. (2012) (62%). Application of combined zeolite and PAC/alum amendments reduced  $\text{NH}_4\text{-N}$  concentrations in runoff to approximately those of the control soil ( $3.37 \text{ mg L}^{-1}$ ) for dairy slurry ( $5.25 \text{ mg L}^{-1}$ ) and DSW ( $3.37 \text{ mg L}^{-1}$ ) but not for pig slurry ( $13.95 \text{ mg L}^{-1}$ ).

The physical composition of the three wastes (Table 1) and their appearance on the grassed soil was quite different. Whereas 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 approximately 25 mm 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  $\text{NH}_4\text{-N}$  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  $\text{NH}_4\text{-N}$  removal as measured for dairy slurry. We are not sure why the  $\text{NH}_4\text{-N}$  runoff removal rate for DSW was so high, but it may be possible that the alum 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  $\text{NH}_4\text{-N}$  concentrations for pig and dairy slurries were  $1800 \text{ mg L}^{-1}$ , whereas that of the DSW was much lower at  $164 \text{ mg L}^{-1}$ , and this also may have influenced concentrations of  $\text{NH}_4\text{-N}$  in runoff.

Loss of  $\text{NH}_4\text{-N}$  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 volatilization, 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 volatilization, Lefcourt 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 with 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 with the unamended controls, with most of the losses occurring in the initial 24-h period and at a reduced rate thereafter. Although the modes of ammonia capture were different for both types of amendments (acidification for alum [Bussink et al., 1994] and availability of  $\text{NH}_4\text{-N}$  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 runoff boxes, 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 before landspreading to facilitate reduced ammonia volatilization.

## Suspended Sediment in Runoff

Suspended sediment in runoff from the control soil was  $0.99 \text{ kg ha}^{-1}$ , and the largest increases after application of unamended wastes were for dairy slurry ( $19.5 \text{ kg ha}^{-1}$ ), followed by DSW ( $4.7 \text{ kg ha}^{-1}$ ) and pig slurry ( $4.0 \text{ kg ha}^{-1}$ ). The large increase for dairy slurry is consistent with its relatively high DM content compared with 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 dairy and pig slurries when amended with dual zeolite and PAC but were reduced for DSW when amended with dual zeolite and alum. This suggests that SS reduction is predominantly due to the 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 a corresponding lower P adsorption capacity than either the silt or clay fractions (Hansen et al., 2002).

## Cost Analysis of Amendments

A preliminary cost analysis on the use of dual zeolite and PAC/alum amendments indicates that high costs, particularly the cost of zeolite, may be a prohibitive factor regarding their

widespread application. Taking the cost of amendments only (without the ancillary costs of storage, application, mixing, and spreading) at €1,150  $\text{t}^{-1}$  for zeolite (in Ireland), €480  $\text{t}^{-1}$  for PAC, and €250  $\text{tonne}^{-1}$  for alum, the costs per cubic meter of applied slurry based on application rates used in this study are €190 for dairy slurry, €188 for pig slurry, and €84 for DSW. These compare with estimated costs per cubic meter 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 the 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.

## Acknowledgments

The authors thank Zeolite Ireland Ltd.; Drs. David Wall, Stan Lalor, and Karen Daly for assistance; and the anonymous reviewers for their very valuable comments during preparation of this manuscript. Use of a product or brand does not constitute an endorsement.

## References

- Alaoui, A., U. Caduff, H.H. Gerke, and R. Weingartner. 2011. A preferential flow effects on infiltration and runoff in grassland and forest soils. *Vadose Zone J.* 10:367–377. doi:10.2136/vzj2010.0076
- Allen, B.L., and A.P. Mallarino. 2008. Effect of liquid swine manure rate, incorporation, and timing of rainfall on phosphorus loss with surface runoff. *J. Environ. Qual.* 37:125–137. doi:10.2134/jeq2007.0125
- APHA. 2005. Standard methods for the examination of water and wastewater. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC.
- Brennan, R.B., O. Fenton, M. Rodgers, and M.G. Healy. 2011. Evaluation of chemical amendments to control phosphorus losses from dairy slurry. *Soil Use Manage.* 27:238–246. doi:10.1111/j.1475-2743.2011.00326.x
- Brennan, R.B., M.G. Healy, J. Grant, T.G. Ibrahim, and O. Fenton. 2012. Incidental event phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry. *Sci. Total Environ.* 441:132–140. doi:10.1016/j.scitotenv.2012.09.078
- British Standards Institution. 1990a. British standard methods of test for soils for civil engineering purposes: Determination of particle size distribution. BS 1377:1990:2. BSI, London.
- British Standards Institution. 1990b. Determination by mass-loss on ignition: British standard methods of test for soils for civil engineering purposes. Chemical and electro-chemical tests. BS 1377:1990:3. BSI, London.
- Bussink, D.W., J.F.M. Huijsmans, and J.J.M.H. Ketelaars. 1994. Ammonia volatilization from nitric-acid-treated cattle slurry surface applied to grassland. *Neth. J. Agric. Sci.* 42:293–309.
- Chadwick, D., S. Sommer, R. Thorman, D. Fangueiro, L. Cardenas, B. Amon, and T. Misselbrook. 2011. Manure management: Implications for greenhouse gas emissions. *Anim. Feed Sci. Technol.* 166-167:514–531. doi:10.1016/j.anifeedsci.2011.04.036
- Department of Agriculture, Food and the Marine. 2013. Food harvest 2020: A vision for Irish agri-food and fisheries. <https://www.agriculture.gov.ie/agri-foodindustry/foodharvest2020/> (accessed 28 Nov. 2014).
- Dodds, W.K., J.R. Jones, and E.B. Welch. 1998. Suggested classification of stream trophic state: Distributions of temperate stream types by chlorophyll, total nitrogen, and phosphorus. *Water Res.* 32:1455–1462. doi:10.1016/S0043-1354(97)00370-9
- Elliott, H., R.C. Brandt, and G. O'Connor. 2005. Runoff phosphorus losses from surface-applied biosolids. *J. Environ. Qual.* 34:1632–1639. doi:10.2134/jeq2004.0467
- Englert, H., and J. Rubio. 2005. Characterization and environmental application of a Chilean natural zeolite. *Int. J. Miner. Process.* 75:21–29. doi:10.1016/j.minpro.2004.01.003
- Hanrahan, L.P., W.E. Jokela, and J.R. Knapp. 2009. Dairy diet phosphorus and rainfall timing effects on runoff phosphorus from land-applied manure. *J. Environ. Qual.* 38:212–217. doi:10.2134/jeq2007.0672
- Hart, M.R., B.F. Quin, and M.L. Nguyen. 2004. Phosphorus runoff from agricultural land and direct fertilizer effects: A review. *J. Environ. Qual.* 33:1954–1972. doi:10.2134/jeq2004.1954
- Hansen, N.C., T.C. Daniel, A.N. Sharpley, and J.L. Lemunyon. 2002. The fate and transport of phosphorus in agricultural systems. *J. Soil Water Conserv.* 57:408–417.
- Heathwaite, A.L., P.J. Johnes, and N.E. Peters. 1996. Trends in nutrients and water quality. *Hydrol. Processes* 10:263–293. doi:10.1002/(SICI)1099-1085(199602)10:2<263::AID-HYP441>3.0.CO;2-K
- Heathwaite, A., and R. Dils. 2000. Characterising phosphorus loss in surface and subsurface hydrological pathways. *Sci. Total Environ.* 251–252:523–538. doi:10.1016/S0048-9697(00)00393-4
- Kalbasi, M., and K.G. Karthikeyan. 2004. Phosphorus dynamics in soils receiving chemically treated dairy manure. *J. Environ. Qual.* 33:2296–2305. doi:10.2134/jeq2004.2296
- Kleinman, P.J.A., A.N. Sharpley, T.L. Veith, R.O. Maguire, and P.A. Vadas. 2004. Evaluation of phosphorus transport in surface runoff from packed soil boxes. *J. Environ. Qual.* 33:1413–1423. doi:10.2134/jeq2004.1413
- Kleinman, P., D. Sullivan, A. Wolf, R. Brandt, Z. Dou, H. Elliott, J. Kovar, A. Leytem, R. Maguire, P. Moore, L. Saporito, A. Sharpley, A. Shober, T. Sims, J. Toth, G. Toor, H. Zhang, and T. Zhang. 2007. Selection of a water-extractable phosphorus test for manures and biosolids as an indicator of runoff loss potential. *J. Environ. Qual.* 36:1357–1367. doi:10.2134/jeq2006.0450
- Kröger, R., E.J. Dunne, J. Novak, K.W. King, E. McLellan, D.R. Smith, J. Strock, K. Boomer, M. Tomer, and G.B. Noe. 2013. Downstream approaches to phosphorus management in agricultural landscapes: Regional applicability and use. *Sci. Total Environ.* 442:263–274. doi:10.1016/j.scitotenv.2012.10.038
- Lefcourt, A.M., and J.J. Meisinger. 2001. Effect of adding alum or zeolite to dairy slurry on ammonia volatilization and chemical composition. *J. Dairy Sci.* 84:1814–1821. doi:10.3168/jds.S0022-0302(01)74620-6
- McBride, M.B. 2000. Chemisorption and precipitation reactions. In: M.E. Sumner, editor, *Handbook of soil science*. CRC Press, Boca Raton, FL. p. B-265–B-302.
- McDowell, R.W., B.J.F. Biggs, and A.N. Sharpley. 2004. Connecting phosphorus loss from agricultural landscapes to surface water quality. *Chem. Ecol.* 20:1–40. doi:10.1080/02757540310001626092
- McDowell, R.W., and D.P. Hamilton. 2013. Nutrients and eutrophication: Introduction. *Mar. Freshwater Res.* 64:3–6.
- McDowell, R., and A. Sharpley. 2002. Phosphorus transport in overland flow in response to position of manure application. *J. Environ. Qual.* 31:217–227. doi:10.2134/jeq2002.2170
- McDowell, R., A. Sharpley, and G. Folmar. 2001. Phosphorus export from an agricultural watershed. *J. Environ. Qual.* 30:1587–1595. doi:10.2134/jeq2001.3051587x
- Meisinger, J.J., A.M. Lefcourt, J.A.S. Van Kessel, and V. Wilkerson. 2001. Managing ammonia emissions from dairy cows by amending slurry with alum or zeolite or by diet modification. *Sci. World J.* 1(S2):860–865. doi:10.1100/tsw.2001.100
- Miller, N., J.N. Quinton, E. Barberis, and M. Presta. 2009. Variability in the mobilization of sediment and phosphorus across 13 European soils. *J. Environ. Qual.* 38:742–750. doi:10.2134/jeq2008.0041
- Misselbrook, T.H., K.A. Smith, R.A. Johnson, and B.F. Pain. 2002. SE: Structures and environment. *Biosyst. Eng.* 81:313–321.
- Moore, P.A., and D.R. Edwards. 2007. Long-term effects of poultry litter, alum-treated litter, and ammonium nitrate on phosphorus availability in soils. *J. Environ. Qual.* 36:163–174. doi:10.2134/jeq2006.0009
- Morgan, M. 1941. The universal soil testing system. Bulletin 4. Connecticut Agricultural Experimental Station, New Haven, CT.
- Nguyen, M., and C. Tanner. 1998. Ammonium removal from wastewaters using natural New Zealand zeolites. *N. Z. J. Agric. Res.* 41:427–446. doi:10.1080/00288233.1998.9513328
- Nolan, T., S.M. Troy, S. Gilkinson, P. Frost, S. Xie, X. Zhan, C. Harrington, M.G. Healy, and P.G. Lawlor. 2012. Economic analyses of pig manure treatment options in Ireland. *Bioresour. Technol.* 105:15–23. doi:10.1016/j.biortech.2011.11.043

- O'Rourke, S.M., R.H. Foy, C.J. Watson, and A. Gordon. 2012. Assessment of co-blending water treatment residual with dairy manure to reduce phosphorus concentrations in run-off in Northern Ireland. *Soil Use Manage.* 28:157–166. doi:10.1111/j.1475-2743.2012.00397.x
- Preedy, N., K. McTiernan, R. Matthews, L. Heathwaite, and P. Haygarth. 2001. Rapid incidental event phosphorus transfers from grassland. *J. Environ. Qual.* 30:2105–2112. doi:10.2134/jeq2001.2105
- Quinton, J.N., and J.A. Catt. 2007. Enrichment of heavy metals in sediment resulting from soil erosion on agricultural fields. *Environ. Sci. Technol.* 41:3495–3500. doi:10.1021/es062147h
- Regan, J.T., M. Rodgers, M.G. Healy, L. Kirwan, and O. Fenton. 2010. Determining phosphorus and sediment release rates from five Irish tillage soils. *J. Environ. Qual.* 39:185–192. doi:10.2134/jeq2008.0514
- Serrenho, A., O. Fenton, P.N.C. Murphy, J. Grant, and M.G. Healy. 2012. Effect of chemical amendments to dairy soiled water and time between application and rainfall on phosphorus and sediment losses in runoff. *Sci. Total Environ.* 430:1–7. doi:10.1016/j.scitotenv.2012.04.061
- Sharpley, A.N., W.J. Gburek, G. Folmar, and H.B. Pionke. 1999. Sources of phosphorus exported from an agricultural watershed in Pennsylvania. *Agric. Water Manage.* 41:77–89. doi:10.1016/S0378-3774(99)00018-9
- Sharpley, A., and P. Kleinman. 2003. Effect of rainfall simulator and plot scale on overland flow and phosphorus transport. *J. Environ. Qual.* 32:2172–2179. doi:10.2134/jeq2003.2172
- Smith, K.A., D.R. Jackson, and T.J. Pepper. 2001a. Nutrient losses by surface run-off following the application of organic manures to arable land. 1. Nitrogen. *Environmental Pollution (Barking, Essex: 1987)* 112:41–51.
- Smith, D.R., P.A. Moore, Jr., C.L. Griffis, T.C. Daniel, D.R. Edwards, and D.L. Boothe. 2001b. Effects of alum and aluminum chloride on phosphorus runoff from swine manure. *J. Environ. Qual.* 30:992–998. doi:10.2134/jeq2001.303992x
- Sommer, S., and N. Hutchings. 2001. Ammonia emission from field applied manure and its reduction—invited paper. *Eur. J. Agron.* 15:1–15. doi:10.1016/S1161-0301(01)00112-5
- Sommer, S.G., S. Genermont, P. Cellier, N.J. Hutchings, J.E. Olesen, and T. Morvan. 2003. Processes controlling ammonia emission from livestock slurry in the field. *Eur. J. Agron.* 19:465–486. doi:10.1016/S1161-0301(03)00037-6
- Thomas, G.W. 1996. Soil pH and soil acidity. In: D.L. Sparks, editor, *Methods of soil analysis. Part 3. Chemical methods.* SSSA, Madison, WI. p. 475–490.
- Torbert, H.A., K.W. King, and R.D. Harmel. 2005. Impact of soil amendments on reducing phosphorus losses from runoff in sod. *J. Environ. Qual.* 34:1415–1421. doi:10.2134/jeq2004.0481
- Vogel, A.I. 1989. *A textbook of quantitative chemical analysis.* ELBS Publication, London. p. 487–488.
- Wall, D.P., P. Jordan, A.R. Melland, P.-E. Mellander, S. Mechan, and G. Shortle. 2013. Forecasting the decline of excess soil phosphorus in agricultural catchments. *Soil Use Manage.* 29:147–154. doi:10.1111/j.1475-2743.2012.00413.x
- Widiastuti, N., H. Wu, H.M. Ang, and D. Zhang. 2011. Removal of ammonium from greywater using natural zeolite. *Desalination* 277:15–23. doi:10.1016/j.desal.2011.03.030
- Williams, J.D., D.E. Wilkins, D.K. McCool, L.L. Baarstad, and B.L. Kleoer. 1998. A new rainfall simulator for use in low energy rainfall areas. *Appl. Eng. Agric.* 14:243–247. doi:10.13031/2013.19385