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.

Published September 16, 2015

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and Edwards, 2007). In contrast to most studies, Brennan et al. (2012) tested the effect of polyaluminum chloride (PAC) \([\text{Aln(OH)}m\text{Cl}_{n-m}; 10\% \text{ Al}_2\text{O}_3]\), alum \([\text{Al}_2(\text{SO}_4)_n\cdot m\text{H}_2\text{O}; 8\% \text{ Al}_2\text{O}_3]\), or lime \([\text{Ca(OH)}_2]\) 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 montmorillonite) 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 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 to 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 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-µm 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 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°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 Al\(_2\)O\(_3\), BaO, Fe\(_2\)O\(_3\), MnO, TiO\(_2\), and SrO using inductively coupled plasma mass spectrometry; CaO, MgO, K\(_2\)O, and Na\(_2\)O using atomic adsorption spectrometry; P\(_2\)O\(_5\) by colorimetry; and SiO\(_2\) by fusion (Vogel, 1989).

#### Soil

Soil P 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 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 a 0.45-µm filter paper, and measuring the P colorimetrically.

### 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 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°C for 12 h before the experimental onset. Triplicate samples of each waste were tested for TP, DRP, TN, NH\(_4\)–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.

<table>
<thead>
<tr>
<th>Waste type</th>
<th>TP (mg L(^{-1}))</th>
<th>DRP (mg L(^{-1}))</th>
<th>TN (mg L(^{-1}))</th>
<th>NH(_4)–N (mg L(^{-1}))</th>
<th>pH</th>
<th>DM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dairy slurry</td>
<td>563 ± 55</td>
<td>18 ± 4</td>
<td>4174 ± 554</td>
<td>1800 ± 16</td>
<td>7.78 ± 0.03</td>
<td>8.0 ± 0.1</td>
</tr>
<tr>
<td>Pig slurry</td>
<td>619 ± 30</td>
<td>42 ± 1</td>
<td>2648 ± 242</td>
<td>1814 ± 87</td>
<td>7.49 ± 0.05</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td>Dairy-soiled water</td>
<td>52 ± 11</td>
<td>17 ± 1</td>
<td>748 ± 76</td>
<td>163.7 ± 3.0</td>
<td>6.89 ± 0.01</td>
<td>0.7 ± 0.3</td>
</tr>
</tbody>
</table>

† 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% SiO₂) and aluminum (10.4% Al₂O₃) (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 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 (PO₄³⁻P) and N (NH₄⁻N) from the three types of wastes was first investigated using a multipoint Langmuir isotherm (McBride, 2000):

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

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 provides an estimate of the maximum adsorption capacity of the zeolite (g kg⁻¹).

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 for DRP.

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 NH₄⁻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 NH₄⁻N by adding 25 mL of the supernatant to 500 mL of 0.1 mol L⁻¹ 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 NH₄⁻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 NH₄⁻N removal: (i) PAC, comprising 10% Al₂O₃ to the dairy slurry at five Al:TP stoichiometric ratios between 0.5:1 and 1.5:1; (ii) PAC, comprising 10% Al₂O₃ to the pig slurry at five Al:TP stoichiometric ratios between 0.3:1 and 1.25; and (iii) alum, comprising Al₃(PO₄)₂·18H₂O 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 NH₄⁻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⁻¹ DM to the dairy slurry, 6 g g⁻¹ DM to the pig slurry, and 10 g g⁻¹ 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⁻¹ for pig and dairy slurries and 50 m³ 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.

Runoff Boxes and Rainfall Simulation

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). Mains water supply used in the rainfall simulations had a DRP concentration of <0.005 mg L⁻¹, a pH of 7.7 ± 0.2, and an electrical conductivity (measured using an LF 96 Conductivity Meter, WTW) of 0.435 dS m⁻¹.

This experiment used laboratory runoff boxes (1 m long by 0.225 m wide 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.

<table>
<thead>
<tr>
<th>Al₂O₃</th>
<th>BaO</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>SrO</th>
<th>Loss in ignition at 1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.4</td>
<td>0.03</td>
<td>0.90</td>
<td>0.01</td>
<td>66.7</td>
<td>1.57</td>
<td>0.52</td>
<td>4.73</td>
<td>0.86</td>
<td>0.06</td>
<td>&lt;0.001</td>
<td>0.04</td>
<td>14.1</td>
</tr>
</tbody>
</table>
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 mm h⁻¹, were applied to the same soil 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, NH₄⁻N, TON, and NO₃⁻N. Nitrate-N was calculated by subtracting NO₂⁻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, qₘₐₓ, ranged from 0.06 (pig slurry) to 0.31 (dairy slurry) mg P g⁻¹ (PO₄-P) and from 0.74 (DSW) to 7.88 (pig slurry) mg N g⁻¹ (NH₄-N). The optimum combined amendment application rates for reduction of PO₄-P and NH₄-N for dairy slurry were 2 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 g g⁻¹ DM of zeolite with a stoichiometric PAC ratio of 1:1 (Al:TP) and for DSW were 10 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 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 NO₃⁻N, were highest for dairy slurry, followed by pig slurry and DSW (Table 3). The FWMCs of TN, NH₄⁻N, and NO₃⁻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, NH₄⁻N, and NO₃⁻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 NO₃⁻N concentrations in runoff below those of unamended wastes by 49% for dairy slurry (325–167 µg L⁻¹), 31% for pig slurry (168–115 µg L⁻¹), and 38% for DSW (42–26 µg L⁻¹).

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) 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 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 (R² =
and to a lesser extent for pig slurry ($R^2 = 0.64$) and DSW ($R^2 = 0.50$) (Fig. 4).

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.

<table>
<thead>
<tr>
<th>Waste application†</th>
<th>TP‡</th>
<th>PP</th>
<th>TDP</th>
<th>DRP</th>
<th>DUP</th>
<th>TN</th>
<th>NH$_4^+$-N</th>
<th>NO$_2^-$-N</th>
<th>NO$_3^-$-N</th>
<th>SS</th>
<th>pH</th>
<th>% reduction (+) increase from unamended slurry pH in runoff</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control soil</td>
<td>0.87</td>
<td>0.43</td>
<td>0.44</td>
<td>0.19</td>
<td>0.25</td>
<td>9.64</td>
<td>3.37</td>
<td>9</td>
<td>36</td>
<td>27</td>
<td>6.43</td>
<td>–</td>
</tr>
<tr>
<td>D(U)</td>
<td>8.68</td>
<td>6.44</td>
<td>2.23</td>
<td>1.16</td>
<td>1.07</td>
<td>41.00</td>
<td>16.53</td>
<td>380</td>
<td>325</td>
<td>535</td>
<td>6.73</td>
<td>–</td>
</tr>
<tr>
<td>D(CA)</td>
<td>2.14</td>
<td>0.77</td>
<td>1.37</td>
<td>0.60</td>
<td>0.28</td>
<td>25.54</td>
<td>7.11</td>
<td>179</td>
<td>180</td>
<td>198</td>
<td>6.30</td>
<td>–</td>
</tr>
<tr>
<td>D(A)</td>
<td>1.11</td>
<td>0.28</td>
<td>0.83</td>
<td>0.35</td>
<td>0.48</td>
<td>18.08</td>
<td>5.25</td>
<td>131</td>
<td>167</td>
<td>143</td>
<td>6.37</td>
<td>–</td>
</tr>
<tr>
<td>P(U)</td>
<td>5.28</td>
<td>1.69</td>
<td>3.59</td>
<td>2.60</td>
<td>0.99</td>
<td>41.02</td>
<td>26.10</td>
<td>42</td>
<td>168</td>
<td>101</td>
<td>6.58</td>
<td>–</td>
</tr>
<tr>
<td>P(CA)</td>
<td>2.00</td>
<td>1.06</td>
<td>0.95</td>
<td>0.60</td>
<td>0.35</td>
<td>35.56</td>
<td>26.65</td>
<td>62</td>
<td>175</td>
<td>52</td>
<td>6.67</td>
<td>1.3</td>
</tr>
<tr>
<td>P(A)</td>
<td>1.00</td>
<td>0.49</td>
<td>0.51</td>
<td>0.22</td>
<td>0.29</td>
<td>22.48</td>
<td>13.95</td>
<td>42</td>
<td>115</td>
<td>57</td>
<td>6.21</td>
<td>–</td>
</tr>
<tr>
<td>DSW(U)</td>
<td>1.84</td>
<td>1.03</td>
<td>0.81</td>
<td>0.35</td>
<td>0.46</td>
<td>25.95</td>
<td>12.43</td>
<td>11</td>
<td>42</td>
<td>112</td>
<td>6.08</td>
<td>–</td>
</tr>
<tr>
<td>DSW(CA)</td>
<td>1.57</td>
<td>0.59</td>
<td>0.98</td>
<td>0.49</td>
<td>0.49</td>
<td>23.98</td>
<td>8.46</td>
<td>13</td>
<td>31</td>
<td>48</td>
<td>5.93</td>
<td>–</td>
</tr>
<tr>
<td>DSW(A)</td>
<td>0.92</td>
<td>0.54</td>
<td>0.38</td>
<td>0.17</td>
<td>0.21</td>
<td>14.33</td>
<td>3.37</td>
<td>14</td>
<td>26</td>
<td>85</td>
<td>6.95</td>
<td>14.3</td>
</tr>
</tbody>
</table>

† D(A), dairy slurry amended with zeolite at 2 g g$^{-1}$ dry matter (DM) (160 kg m$^{-2}$) and polyaluminum chloride (PAC) at 1:2.5:1 Al:total P (TP) (704 mg L$^{-1}$); D(CA), dairy slurry amended with PAC at 1:2.5:1 Al:TP (704 mg L$^{-1}$); DSW(A), dairy-soiled water amended with zeolite at 10 g g$^{-1}$ DM (70 kg m$^{-2}$) and alum at 5:1 Al:TP (260 mg L$^{-1}$); DSW(CA), dairy-soiled water amended with alum at 5:1 Al:TP (260 mg L$^{-1}$); DSW(U), unamended dairy-soiled water; D(U), unamended dairy slurry; P(A), pig slurry amended with zeolite at 6 g g$^{-1}$ DM (156 kg m$^{-2}$) and PAC at 1:1 Al:TP (619 mg L$^{-1}$); P(CA), pig slurry amended with PAC at 1:1 Al:TP (619 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.
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 NH$_4$–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).
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\(^{-1}\) for the control soil. 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 d of intermittent rainfall ranging in intensity from 0.2 to 3 mm h\(^{-1}\) rainfall in a lysimeter 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\(^{-1}\)) study, reductions in TP for dairy slurry are dominated byPP of dairy waste and a simulated rainfall event. In the current

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\(^{-1}\) 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 TP reduction of approximately 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 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 NH$_4^-$-N compared with 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 with 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. 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 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 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 pig and dairy slurries were 1800 mg L$^{-1}$, whereas 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, 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 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 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 0.09 kg ha$^{-1}$, and the largest increases after 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 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 t⁻¹ for zeolite (in Ireland), €480 t⁻¹ for PAC, and €250 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

Bussink, D.W., J.E.M. Huisjmans, and J.J.M.H. Ketelaars. 1994. Ammonia volatilization from nitric-acid-treated cattle slurry surface applied to agricultural wastes is limited.


