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

8 J.G. Murnane^{1,2}, R.B. Brennan¹, M.G. Healy^{1*}, O. Fenton³

9 ¹Civil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of
10 Ireland.

11 ²Civil Engineering and Materials Science, University of Limerick, Co. Limerick, Rep.
12 of Ireland.

13 ³Teagasc, Johnstown Castle, Environment Research Centre, Co Wexford, Rep. of
14 Ireland

15
16 *Corresponding author. Tel: +353 91 495364; fax: +353 91 494507. E-mail address:
17 mark.healy@nuigalway.ie

18
19 **Abbreviation list:**

20 DSW – Dairy soiled water

21 PAC – Poly-aluminum chloride

22 FWMC – Flow-weighted mean concentration

23 DRP – Dissolved reactive phosphorus

24

25

26

27 **Abstract**

28 Diffuse pollutant losses containing phosphorus (P), nitrogen (N) and suspended solids
29 (SS) can occur when agricultural wastes are applied to soil. This study aimed to
30 mitigate P, N and SS losses in runoff from grassed soils, onto which three types of
31 agricultural wastes, dairy slurry, pig slurry and dairy soiled water (DSW), were
32 applied by combining amendments of either zeolite and poly-aluminum chloride
33 (PAC) with dairy and pig slurries, or zeolite and alum with DSW. Four treatments
34 were investigated in rainfall simulation studies: (1) control soil (2) agricultural wastes
35 (3) dairy and pig slurries amended with PAC; DSW amended with alum, and (4) dairy
36 and pig slurries amended with zeolite and PAC; DSW amended with zeolite and alum.
37 Our data showed that combined amendments of zeolite and PAC applied to dairy and
38 pig slurries reduced total phosphorus (TP) in runoff by 87% and 81%, respectively,
39 compared to unamended slurries. A combined amendment of zeolite and alum applied
40 to DSW reduced TP in runoff by 50% compared to unamended DSW. The
41 corresponding reductions in total nitrogen (TN) were 56% for dairy slurry and 45%
42 for both pig slurry and DSW. Use of combined amendments reduced SS in runoff by
43 73% and 44% for dairy and pig slurries, and 25% for DSW compared to unamended
44 controls, but were not significantly different from those using chemical amendments
45 only. The findings of this study are that combined amendments of zeolite and either
46 PAC or alum reduce TP and TN losses in runoff to a greater extent than use of single
47 PAC or alum amendments, and are most effective when used with dairy slurry and pig
48 slurry but less effective when used with DSW.

49

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

52

53 **1. Introduction**

54

55 Excessive application of agricultural waste to soils may have environmental impacts,
56 including phosphorus (P), nitrogen (N) and suspended solids (SS) losses, and increase
57 greenhouse gas emissions (Smith et al., 2001a; Chadwick et al., 2011; Kröger et al.,
58 2013; McDowell and Hamilton, 2013). Loss of P, N and SS in overland flow is
59 affected by the time interval between surface application and rainfall events (Allen
60 and Mallarino, 2008; Hanrahan et al., 2009), antecedent hydrologic conditions
61 (Brennan et al., 2012), flow path length (McDowell and Sharpley, 2002), surface
62 slope (Alaoui et al., 2011), soil type (Wall et al., 2013), and the short and long-term
63 effects of agricultural waste application to the soil structure (McDowell et al., 2004).
64 Event P losses in surface runoff following land application of agricultural wastes may
65 be dominated by particulate phosphorus (PP) (Preedy et al., 2001) or by dissolved
66 phosphorus, depending on individual circumstances such as grazing animals, type of
67 stock, topography and degree of exposure of the soil to rainfall events (Hart et al.,
68 2004), while most of the permanent P losses in surface runoff from soils are in
69 dissolved form (Heathwaite and Dils, 2000). Nitrogen losses are dominated by
70 ammonium (NH₄-N) (Heathwaite et al., 1996; Smith et al., 2001a). Suspended
71 sediment is an important carrier of contaminants (Quinton and Catt, 2007) and,
72 depending on the soil type and rainfall characteristics, P enriched soil particles may
73 increase the proportion of PP in surface runoff (McDowell et al., 2001; Miller et al.,
74 2009).

75

76 With European policy advocating farm intensification (Department of Agriculture,
77 Food and the Marine, 2013), farmers may have no choice but to spread agricultural
78 waste on land with a high soil P. Land spreading remains the most economical and
79 widespread disposal practice for agricultural wastes (e.g. Nolan et al., 2012). Use of
80 chemical amendments applied to agricultural waste to reduce P losses in surface
81 runoff following land application has been shown to be effective (Smith et al., 2001b;
82 Kalbasi and Karthikeyan, 2004; Moore and Edwards, 2007). In contrast to most
83 studies, Brennan et al. (2012) tested the effect of either poly-aluminum chloride
84 (PAC; $Al_n(OH)_mCl_{3n-m}$; 10% Al_2O_3), alum ($Al_2(SO_4)_3 \cdot nH_2O$; 8% Al_2O_3), or lime
85 ($Ca(OH)_2$) on both P and N losses. They found that the three chemicals did not have a
86 significant effect on N losses following the first rainfall event two days after slurry
87 application to grassed plots.

88

89 Zeolite has been shown to be effective in adsorbing N from synthetic wastes (Englert
90 and Rubio, 2005; Widiastuti et al., 2011) and agricultural wastes (Nguyen and Tanner,
91 1998). Nguyen and Tanner (1998) found that two types of New Zealand zeolite
92 (clinoptilolite and modernite) removed 62-99% of N in batch adsorption experiments
93 using domestic sewage and synthetic, pig and dairy wastewaters. They found in an
94 infiltration experiment that for a throughput of up to 40 bed volumes, the removal rate
95 of NH_4-N from pig and dairy slurries was over 98% at a hydraulic loading rate (HLR)
96 of 0.47 mm min^{-1} and 50-90% at a HLR of 15.9 mm min^{-1} . Zeolite has also been
97 shown to be effective in reducing ammonia emissions from dairy slurry stored in the
98 holding pit of a 100-cow free stall barn (Meisinger et al., 2001).

99

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

107

108 **2. Materials and Methods**

109

110 **2.1 Chemical and physical analyses**

111 **2.1.1 Agricultural wastes**

112 Total phosphorus (TP) was measured using acid persulphate digestion and dissolved
113 reactive phosphorus (DRP) by centrifuging at 17,970 RCF (relative centrifugal force)
114 for 5 min, filtering through 0.45 µm filters and measuring colorimetrically using a
115 nutrient analyzer (Konelab 20, Thermo Clinical Laboratories Systems, Finland). Total
116 nitrogen (TN) was measured using a BioTector TOC TN TP Analyzer (BioTector
117 Analytical Systems Ltd., Cork, Ireland). Ammonium was extracted from fresh waste
118 by shaking 10 g of waste in 200 mL of 0.1M HCL on a peripheral shaker for 30 min
119 at 200 rpm, centrifuging at 17,970 RCF for 5 min and measuring colorimetrically.

120 Waste pH was measured using a pH probe (WTW, Germany) and dry matter (DM)
121 was measured by drying at 105 °C for 24 h. All parameters were tested in accordance
122 with the standard methods (APHA, 2005).

123

124 **2.1.2 Zeolite**

125 The zeolite was sieved to a particle size of 2.36 – 3.35 mm and analyzed for Al₂O₃,
126 BaO, Fe₂O₃, MnO, TiO₂, and SrO using inductively coupled plasma mass
127 spectrometry (ICP-MS), CaO, MgO, K₂O and Na₂O using atomic adsorption
128 spectrometry (AAS), P₂O₅ by colorimetry and SiO₂ by method of fusion (Vogel,
129 1989).

130

131 **2.1.3 Soil**

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

141

142 **2.1.4 Rainfall simulator runoff**

143 Runoff samples were tested for pH using a pH probe and for SS using vacuum
144 filtration of at least 50 mL of well-mixed, previously unfiltered, subsamples through
145 Whatman GF/C (pore size 1.2 µm) filter paper (APHA, 2005). Sub-samples were
146 filtered through 0.45 µm filters and measured colorimetrically for DRP, NH₄-N, total
147 oxidized nitrogen (TON) and nitrite-N (NO₂-N) using a nutrient analyzer (Konelab
148 20, Thermo Clinical Labsystems, Finland). Unfiltered sub-samples were tested for TP

149 and total dissolved phosphorus (TDP) using acid persulphate digestion, and for TN
150 using a BioTector Analyzer (BioTector Analytical Systems Ltd., Cork, Ireland).

151

152 **2.2 Materials collection and characterization**

153 **2.2.1 Agricultural wastes**

154 Three types of agricultural wastes were collected from the Teagasc Research Centre,
155 Moorepark, Fermoy, Co. Cork. They were: (1) dairy slurry, from a slatted unit
156 housing dairy cows (2) pig slurry, from an integrated pig unit and (3) DSW from a
157 milking parlor washwater collection sump. Dairy soiled water is defined as dairy wash
158 water from hard standing farmyard areas contaminated with livestock feces, urine or
159 silage effluent, fertilizers and parlor washings, which have a DM content < 1% and a
160 5-day biochemical oxygen demand (BOD₅) < 2,500 mg L⁻¹. All wastes were
161 homogenized immediately prior to collection by agitating for 30 min using
162 mechanical agitators. The samples were stored in 25 L containers, which were placed
163 in a temperature-controlled room at 11 °C for 12 h prior to the experimental onset.
164 Triplicate samples of each waste were tested for TP, DRP, TN, NH₄-N, pH and DM
165 (Table 1).

166

167 **2.2.2 Zeolite**

168 The zeolite used in this study was of Turkish origin and the sieved zeolite (2.36 – 3.35
169 mm), comprised mainly silica (66.7% SiO₂) and aluminum (10.4% Al₂O₃) (Table 2).

170

171 **2.2.3 Soil**

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

174 10 yr, in Galway City, Republic of Ireland. The soil was a poorly drained sandy loam
175 (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),
176 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%.
177 The soil type is classified as an acid brown earth Cambisol (WRB classification).

178

179 **2.3 Adsorption capacity of zeolite**

180 The ability of zeolite to remove P (PO₄-P) and N (NH₄-N) from the three types of
181 wastes was first investigated using a multi-point Langmuir isotherm (McBride, 2000):

$$182 \quad \frac{C_e}{\frac{x}{m}} = \frac{1}{ab} + \frac{C_e}{b} \quad (1)$$

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

188

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

197

198 **2.4 Optimum zeolite application**

199 Bench-scale tests were used to establish optimum application ratios of zeolite
200 (expressed as g zeolite per g DM of waste) for NH₄-N removal for each of the wastes.
201 Sieved zeolite (2.36 – 3.35 mm) was added (n=3) in amounts ranging from 1 to 15 g
202 to 40 mL of each waste type in 100 mL containers. All containers were sealed and
203 placed on a reciprocating shaker for 24 h at 250 rpm. The samples were then allowed
204 to settle for 1 h, centrifuged at 17,970 RCF for 5 min and tested for NH₄-N by adding
205 25 mL of the supernatant to 500 mL of 0.1M HCL, shaking for 30 min at 200 rpm,
206 filtering through 0.45 µm filter paper and measuring colorimetrically. The optimum
207 application ratio was defined as the mass of zeolite above which there was little or no
208 enhanced rate of NH₄-N removal in the supernatant, or where the volume of zeolite
209 comprised no greater than 10% of the volume of waste.

210

211 To reduce WEP, the following chemicals were mixed with the wastes to which zeolite
212 had been applied at the established optimum ratios for NH₄-N removal: (1) PAC
213 comprising 10% Al₂O₃ to the dairy slurry at five Al:TP stoichiometric ratios between
214 0.5:1 and 1.5:1 (2) PAC comprising 10% Al₂O₃ to the pig slurry at five Al:TP
215 stoichiometric ratios between 0.3:1 and 1.25:1; and (3) alum comprising
216 Al₂(SO₄)₃·18H₂O to the DSW at five Al:TP stoichiometric ratios between 5:1 and
217 12:1. The combination of amendments that produced the best reductions of NH₄-N
218 concentrations and WEP from the wastes were used in the runoff experiments.

219

220 **2.5 Rainfall simulation study**

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

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

232

233 **2.5.1 Runoff boxes and rainfall simulation**

234 The rainfall simulator consisted of a single 1/4HH-SS14SQW nozzle (Spraying
235 Systems Co. Wheaton, IL) attached to a 4.5 m high steel frame and calibrated to an
236 intensity of $9.6 \pm 0.16 \text{ mmh}^{-1}$ and a droplet impact energy of $260 \text{ kJ mm}^{-1} \text{ ha}^{-1}$ at 80%
237 intensity (Regan et al., 2010). Mains water supply used in the rainfall simulations had
238 a DRP concentration of less than 0.005 mg L^{-1} , a pH of 7.7 ± 0.2 and an electrical
239 conductivity (measured using an LF 96 Conductivity Meter, WTW, Germany) of
240 0.435 dS m^{-1} .

241

242 This experiment used laboratory runoff boxes, 1 m long by 0.225 m wide by 0.05 m
243 deep with side walls 25 mm higher than the soil surface and 5 mm diameter drainage
244 holes each located at 0.3 m intervals along the base (Regan et al., 2010). The runoff
245 boxes were positioned at a 10% slope to the horizontal, and all surface runoff was
246 collected at the downstream end using an overflow weir with the crest positioned at
247 the same level as the soil surface. Muslin cloth was placed at the base of each

248 laboratory runoff box to prevent soil loss through the drain holes at the base before
249 packing the soil. Intact grassed cores from the study site were transported to the
250 laboratory and stored at 11 °C prior to testing. All experiments were carried out
251 within 14 d of soil core collection. Immediately prior to the start of each runoff box
252 experiment, each core was trimmed to a typical length of between 450-500 mm and
253 butted against an adjacent core to form a continuous surface of between two and three
254 cores. Molten candle wax was used to seal any gaps between the cores and the sides
255 of the runoff box. The grass on the soil samples was cut to an approximate length of
256 25 mm to simulate freshly cut meadow conditions.

257

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

271

272 **2.5.2 Runoff analysis**

273 Each of the samples taken at 5 min intervals was tested for pH and for SS. Sub-
274 samples, also taken at 5 min intervals, were measured for DRP, NH₄-N, TON and
275 NO₂-N. Nitrate-N was calculated by subtracting NO₂-N from TON. Unfiltered sub-
276 samples, taken at 10, 20 and 30 min after continuous runoff were tested for TP, TDP
277 and TN. Dissolved unreactive phosphorus (DUP) was calculated by subtracting DRP
278 from TDP and PP was calculated by subtracting TDP from TP.

279

280 **2.5.3 Data analysis**

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

286

287 **3. Results**

288

289 **3.1 Adsorption Capacity and bench scale studies**

290 The monolayer adsorption capacity of zeolite, q_{\max} , ranged from 0.06 (pig slurry) to
291 0.31 (dairy slurry) mg P g⁻¹ (PO₄-P) and from 0.74 (DSW) to 7.88 (pig slurry) mg N
292 g⁻¹ (NH₄-N). The optimum combined amendment application rates for reduction of
293 both PO₄-P and NH₄-N for dairy slurry were 2 g g⁻¹ DM of zeolite + a stoichiometric
294 PAC ratio of 1.25:1 (Al:TP). The corresponding rates for pig slurry were 6 g g⁻¹ DM
295 of zeolite + a stoichiometric PAC ratio of 1:1 (Al:TP) and for DSW, 10 g g⁻¹ DM of
296 zeolite + a stoichiometric alum ratio of 5:1 (Al:TP).

297

298 **3.2 Runoff from laboratory rainfall simulation study**

299 **3.2.1 Phosphorus**

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

308

309 **3.2.2 Nitrogen**

310 The FWMC for TN from the control soil ranged from 8.5 (RE1) to 11 mg L⁻¹ (RE3).
311 The TN concentrations in runoff were observed to increase for all unamended slurry
312 applications compared to the control soil ($p<0.001$). Ammonium-N concentrations
313 were highest for pig slurry, followed by dairy slurry and DSW, while TON
314 concentrations in runoff, primarily as NO₃-N, were highest for dairy slurry, followed
315 by pig slurry and DSW (Table 3). The FWMC of TN, NH₄-N and NO₃-N in runoff for
316 chemically amended wastes (without zeolite addition) over the three rainfall events
317 were reduced by 40%, 57% and 45% (dairy slurry), 13%, 0% and 0% (pig slurry), and
318 8%, 32% and 26% (DSW) compared to unamended wastes. Application of combined
319 zeolite and chemical amendments further reduced TN, NH₄-N and NO₃-N
320 concentrations in runoff from all three wastes over the three rainfall events to below
321 those achieved by chemical amendments only (Figure 2). Decreases in TN of
322 amended wastes compared to unamended wastes were significant for all treatments,

323 except for alum-amended DSW and PAC amended pig slurry ($p < 0.001$). The TN
324 concentrations in runoff using dual zeolite and PAC/alum amendments were less than
325 those using PAC/alum amendments only for all wastes ($p < 0.001$). The combined
326 amendments reduced $\text{NO}_3\text{-N}$ concentrations in runoff below those of unamended
327 wastes by 49% for dairy slurry (325 to 167 $\mu\text{g L}^{-1}$), 31% for pig slurry (168 to 115 μg
328 L^{-1}), and 38% for DSW (42 to 26 $\mu\text{g L}^{-1}$).

329

330 **3.2.3 Suspended solids**

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

339

340 The average FWMC of PP in runoff was highly correlated with corresponding SS
341 concentrations for dairy slurry ($R^2 = 0.92$) and to a lesser extent for pig slurry ($R^2 =$
342 0.64) and DSW ($R^2 = 0.50$) (Figure 4).

343

344 **3.2.4 pH**

345 Over the three rainfall events, the average pH in runoff from PAC-amended dairy
346 slurry was lower than unamended dairy slurry (Table 3). There was no significant
347 difference in pH between unamended and PAC-amended pig slurry and unamended

348 and alum-amended DSW (Table 3). The average pH in runoff over the three rainfall
349 events from dairy and pig slurries amended with zeolite and PAC was lower than that
350 for unamended slurries, but was higher in runoff from DSW amended with zeolite and
351 alum.

352

353 **4. Discussion**

354 The amendments used in this study had specific removal capacities, predominantly
355 zeolite for N removal and PAC/alum for P and SS removal. The combinations used
356 were those that produced the best reductions of $\text{NH}_4\text{-N}$ and WEP from the wastes
357 (Section 2.4). The use of packed soil boxes and simulated rainfall is recognized as a
358 practical, if limited, method to assess P transport from grassed and bare soils
359 (Sharpley and Kleinman, 2003; Kleinman et al., 2004).

360

361 **4.1 Phosphorus in runoff**

362 Observed reductions in P using only PAC/alum amendments (without zeolite) were
363 generally consistent with previous studies (Smith et al., 2001b; Elliott et al., 2005;
364 O'Rourke et al., 2012). The average concentrations of TP in runoff following
365 application of unamended dairy slurry increased from 0.87 mg L^{-1} for the control soil
366 to 8.7 mg L^{-1} . This is consistent with the findings of Preedy et al. (2001), who
367 recorded peak TP concentrations of 7 mg L^{-1} from dairy slurry (6% DM) exposed to
368 28 days of intermittent rainfall ranging in intensity from $0.2 - 3 \text{ mm h}^{-1}$ rainfall in a
369 lysimeter plot study. The reduced runoff concentrations in TP and DRP for dairy
370 slurry using PAC at a ratio of 1.25:1 Al:TP (87% and 70%, respectively) were similar
371 to those reported by Hanrahan et al. (2009) (89% and 65%, respectively) at a time
372 interval of 5 d between application of dairy waste and a simulated rainfall event. In

373 the current study, reductions in TP for dairy slurry are dominated by reductions in PP
374 (6.44 to 0.77 mg L⁻¹), and the average FWMC of PP and SS in runoff were related to
375 one another (Figure 4). The comparatively high DM content of dairy slurry compared
376 to the other wastes (Table 1) meant that, when applied to the soil, much of it remained
377 on the surface for the duration of the experiment. This contrasted with the pig slurry
378 and DSW, which infiltrated the soil quite quickly after application because of their
379 lower DM contents. The position of the dairy slurry on the soil facilitated a higher
380 direct exposure to rainfall compared to the other applied wastes, and resulted in higher
381 runoff SS (Figure 3) and PP concentrations (Figure 1). Eroded P-enriched particles
382 can be mobilized by rain splash detachment, flow detachment or dispersion (Miller et
383 al., 2009), and may be transported significant distances (Sharpley et al., 1999). Our
384 results indicate that suspended dairy slurry solids, as opposed to soil solids, may be
385 the principal transport mechanism for runoff P, predominantly as PP, from
386 unamended slurry. The addition of PAC and PAC/zeolite to the dairy slurry reduced
387 SS and PP concentrations. It is likely that release of Al³⁺ flocculants from the PAC
388 reduced the extent of fragmentation of the slurry into primary particles, hence reducing
389 the concentration of SS transported by overland flow. The ratio of PP:TP reduced from
390 0.74 for unamended slurry to 0.36 for PAC amended slurry and 0.25 for combined
391 zeolite and PAC amended dairy slurry, confirming that PAC, and not zeolite, is the most
392 effective of the two amendments in binding PP.

393

394 The SS concentrations in runoff from unamended pig slurry were much lower than
395 those of unamended dairy slurry, as were the TP concentrations. The correlation
396 between PP and SS for pig slurry was not as strong as for dairy slurry (Figure 4). This
397 was likely due to the lower DM content of the pig slurry (Table 1). As a consequence,

398 it is likely that the same opportunity for particle segregation from the slurry was not
399 available and thus PP in runoff was not as prevalent as for dairy slurry (PP:TP =
400 0.32). The addition of PAC amendment only (no zeolite) increased the PP:TP ratio to
401 0.53, while the ratio for dual zeolite and PAC was similar (0.49). The overall DRP
402 removal rates for pig slurry were similar to those of previous studies. In a runoff
403 experiment to evaluate the impact of alum and aluminum chloride on swine manure
404 applied to small grassed plots, Smith et al. (2001b) observed DRP reductions of 4.6
405 mg L⁻¹ in runoff between unamended manure and manure treated with 1:1 Al:TP
406 molar ratio. This represented an 84% reduction in DRP, and is comparable to the 77%
407 reduction measured in the current study using PAC at the same ratio. The removal
408 rates in the current study increased to 92% when combined zeolite and PAC
409 amendments were applied.

410

411 Very few data exist on runoff P concentrations from DSW applied to grassed soil
412 under simulated rainfall conditions. In a study to measure the effects of rainfall events
413 on P and SS losses from a grassed soil, Serrenho et al. (2012) reported an approximate
414 TP reduction of 80% from relatively dilute DSW (DM = 0.2%, TP = 14.2 mg L⁻¹)
415 amended with alum at a stoichiometric ratio of 8.8:1. They reported a weak
416 correlation ($R^2 = 0.15$) between PP and SS in runoff for the unamended DSW, but a
417 high PP:TP ratio of 0.75. In the current study, a lower stoichiometric ratio (5:1) of
418 alum amendment resulted in a lower TP reduction of 15% for a stronger DSW than
419 that of Serrenho et al. (2012) (Table 1). It is likely that application of the higher alum
420 ratio by Serrenho et al. (2012) was more successful in sorbing dissolved P to the soil
421 than in the current study and P-enriched soil particles were then mobilized in runoff.
422 In the current study, both alum and dual zeolite and alum amendments resulted in

423 similar reductions in PP (43% and 48%, respectively) compared to unamended DSW.
424 Use of alum only (no zeolite) did not reduce dissolved P below that of unamended
425 waste. In contrast, dual application of zeolite and alum reduced both DRP and DUP
426 by 53%, indicating that zeolite may have contributed to dissolved P removal in runoff
427 from DSW. The PP:TP ratios for the unamended DSW, alum amended DSW and
428 dual zeolite and alum amended DSW were 0.56, 0.38 and 0.59, respectively. These,
429 combined with the weak correlation between PP and SS in runoff (Figure 4), suggest
430 that dissolved P losses may be just as significant as PP losses for the rates of
431 amendments used.

432

433 **4.2 Nitrogen in runoff**

434 The results of this study confirm the results of previous studies using specific
435 amendments in the treatment of agricultural wastes for N (Nguyen and Tanner, 1998;
436 Widiastuti et al., 2011). The observed reductions in runoff $\text{NH}_4\text{-N}$ compared to
437 unamended wastes were highest for pig slurry, followed by dairy slurry and DSW
438 (Table 3). The reduction in $\text{NH}_4\text{-N}$ in runoff from dairy slurry amended with PAC
439 (57%) compared to unamended dairy slurry was consistent with the findings of
440 Brennan et al., (2012) (62%). Application of combined zeolite and PAC/alum
441 amendments reduced $\text{NH}_4\text{-N}$ concentrations in runoff to approximately those of the
442 control soil (3.37 mg L^{-1}) for dairy slurry (5.25 mg L^{-1}) and DSW (3.37 mg L^{-1}), but
443 not for pig slurry (13.95 mg L^{-1}).

444

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

448 observed that the interaction between the applied manure and runoff water is of
449 primary importance for the loss of pollutants. A high interaction between the grass
450 thatch layer and the manure will greatly reduce the amount of manure that leaves the
451 grassed soil as particles, but also increases the interaction that the runoff water has
452 with the surface area of the manure. Although grass was cropped to approx. 25mm in
453 this study, it is likely that the zeolite benefited from more contact time with the dairy
454 slurry than with either the pig slurry or DSW, and this may have resulted in the lower
455 $\text{NH}_4\text{-N}$ in runoff for the dairy slurry. Conversely, the interaction time between the
456 zeolite and pig slurry may have been insufficient to achieve a similar level of $\text{NH}_4\text{-N}$
457 removal as measured for dairy slurry. We are not sure why the $\text{NH}_4\text{-N}$ runoff removal
458 rate for DSW was so high, but it may be possible that the alum may have sequestered
459 some ammonia, or that pockets of DSW may have pooled on parts of the saturated
460 soil surface, thereby facilitating a higher contact time with the zeolite. The $\text{NH}_4\text{-N}$
461 concentrations for both pig and dairy slurries were 1800 mg L^{-1} , while that of the
462 DSW was much lower at 164 mg L^{-1} , and this also may have influenced
463 concentrations of $\text{NH}_4\text{-N}$ in runoff.

464

465 Loss of $\text{NH}_4\text{-N}$ from land applied wastes is of interest because such losses greatly
466 reduce the fertilizer values of slurry (Misselbrook et al., 2002). More than 50% of
467 applied N can be lost by ammonia volatilization, with close to 50% of these emissions
468 occurring in the first 24 h during and after slurry application (Sommer and Hutchings,
469 2001; Sommer et al., 2003). In an experiment to assess the effects of alum or zeolite
470 addition to dairy slurry on ammonia volatilization, Lefourt and Meisinger (2001) found
471 that 65% of ammonia emissions in unamended slurry occurred within 24 h of
472 exposure. Addition of alum at rates of 2.5% and 6.25% reduced these losses by 58%

473 and 57%, respectively, compared to unamended controls, with most of the losses
474 occurring in the initial 12 h and negligible losses thereafter. In the same experiment,
475 addition of zeolite, also at rates of 2.5% and 6.25%, reduced ammonia emissions by
476 22% and 47%, respectively, compared to the unamended controls, with most of the
477 losses occurring in the initial 24 h period and at a reduced rate thereafter. While the
478 modes of ammonia capture were different for both types of amendments (acidification
479 for alum (Bussink et al., 1994) and availability of $\text{NH}_4\text{-N}$ exchange sites for zeolite),
480 ammoniacal capture occurred mostly within a 24 h period for both amendments, albeit
481 at a much slower rate for zeolite. In the current study, the zeolite and chemical
482 amendments were added immediately before application of the wastewaters to the
483 flumes and it is likely that some ammonia may have volatilized in the initial 48 h
484 period before the rainfall simulation took place. It may be beneficial, therefore, on a
485 practical basis to add the zeolite to the wastewaters at least 24 h and chemicals at least
486 12 h prior to landspreading to facilitate reduced ammonia volatilization.

487

488 **4.3 SS in runoff**

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

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

507

508 **4.4 Cost analysis of amendments**

509 A preliminary cost analysis on use of dual zeolite and PAC/alum amendments
510 indicates that high costs, particularly the cost of zeolite, may be a prohibitive factor in
511 their widespread application. Taking the cost of amendments only (without ancillary
512 costs of storage, application, mixing and spreading) at €1,150 tonne⁻¹ for zeolite (in
513 Ireland), €480 tonne⁻¹ for PAC and €250 tonne⁻¹ for alum, the costs per m³ of applied
514 slurry based on application rates used in this study is €190 for dairy slurry, €188 for
515 pig slurry and €84 for DSW. These compare with estimated costs per m³ of €6.40 for
516 dairy slurry, €5.60 for pig slurry and €0.80 for DSW using PAC/alum amendments
517 only (Brennan et al., 2011). Therefore, the additional cost of using dual zeolite and
518 chemical amendments is significantly higher than use of chemical only (by an order of
519 magnitude in excess of 2 in the case of DSW) and consequently may not be an
520 attractive mitigation option in areas where zeolite is not an indigenous natural
521 material and where purchase costs may be prohibitive. Acknowledging that final costs
522 may vary with location and availability of zeolite, it is nevertheless unlikely that

523 widespread use of dual zeolite and chemical amendments in agricultural wastewaters
524 will be economically sustainable in the short to medium term, and would be better
525 suited to critical source areas (areas where there is a high risk of incidental losses in
526 overland flow), or where land availability for spreading agricultural wastes is limited.

527

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533

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- 684

Table 1 Waste characterization for total phosphorus (TP), dissolved reactive phosphorus (DRP), total nitrogen (TN), ammonium (NH₄-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 ₂ O ₃	BaO	Fe ₂ O ₃	MnO	SiO ₂	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O 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 (NH₄-N), nitrite (NO₂-N), nitrate (NO₃-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)

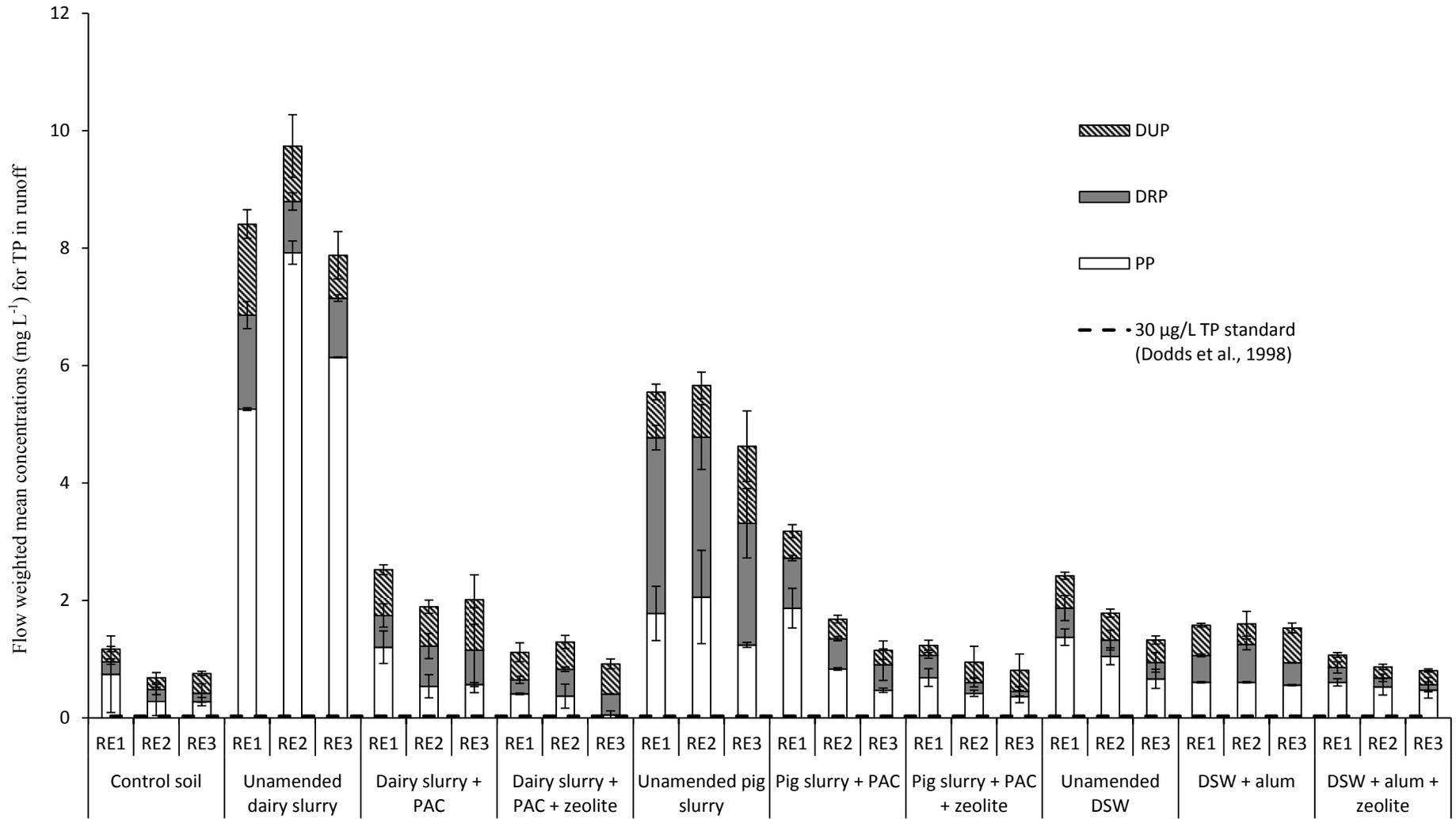


Figure 1: Histogram of flow weighted mean concentrations for total phosphorus (TP) comprising particulate phosphorus (PP), dissolved reactive phosphorus (DRP) and dissolved unreactive phosphorus (DUP) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event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

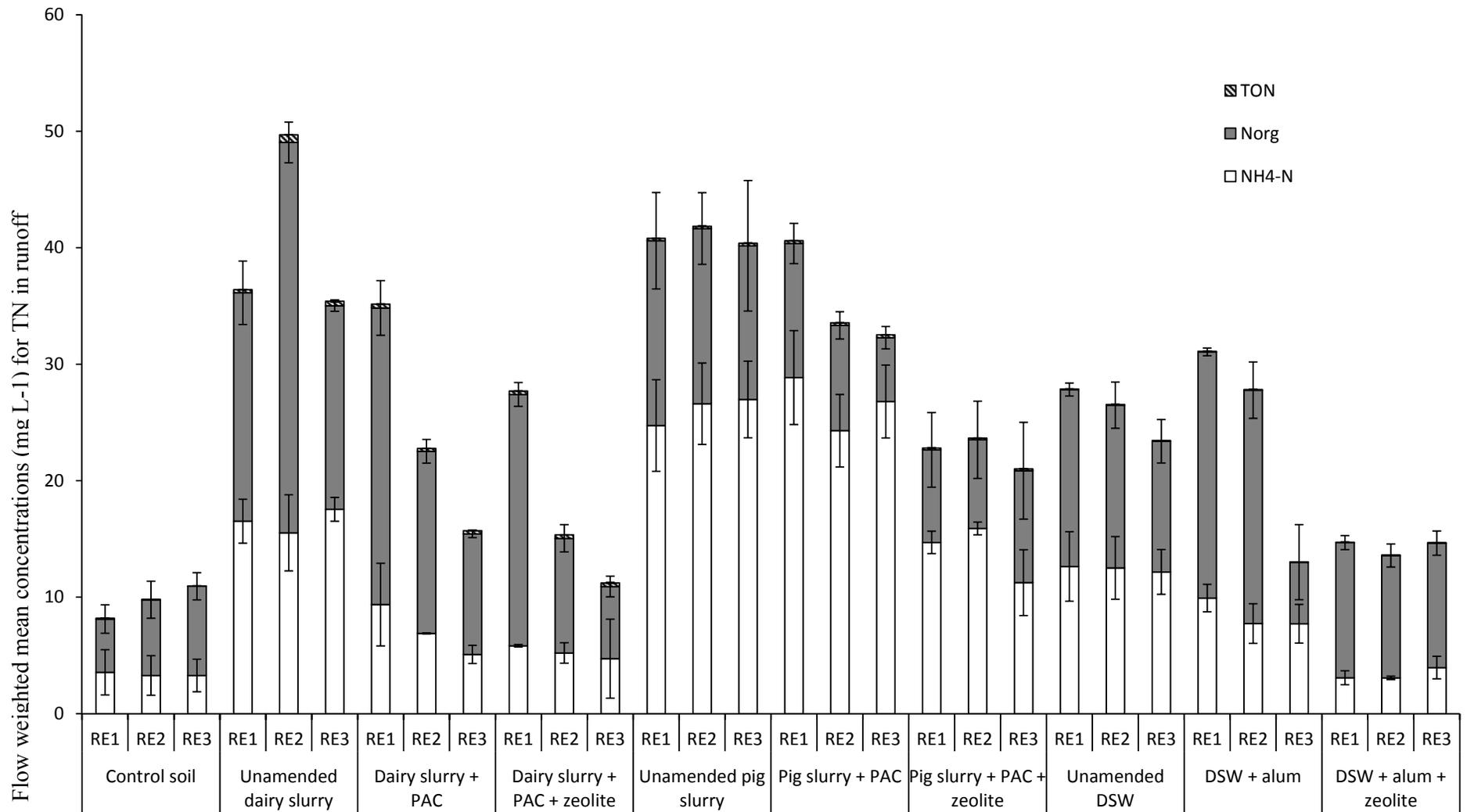


Figure 2: Histogram of flow weighted mean concentrations for total nitrogen (TN) comprising ammonium-N (NH₄-N), organic N (Norg) and total oxidized nitrogen (TON) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h.

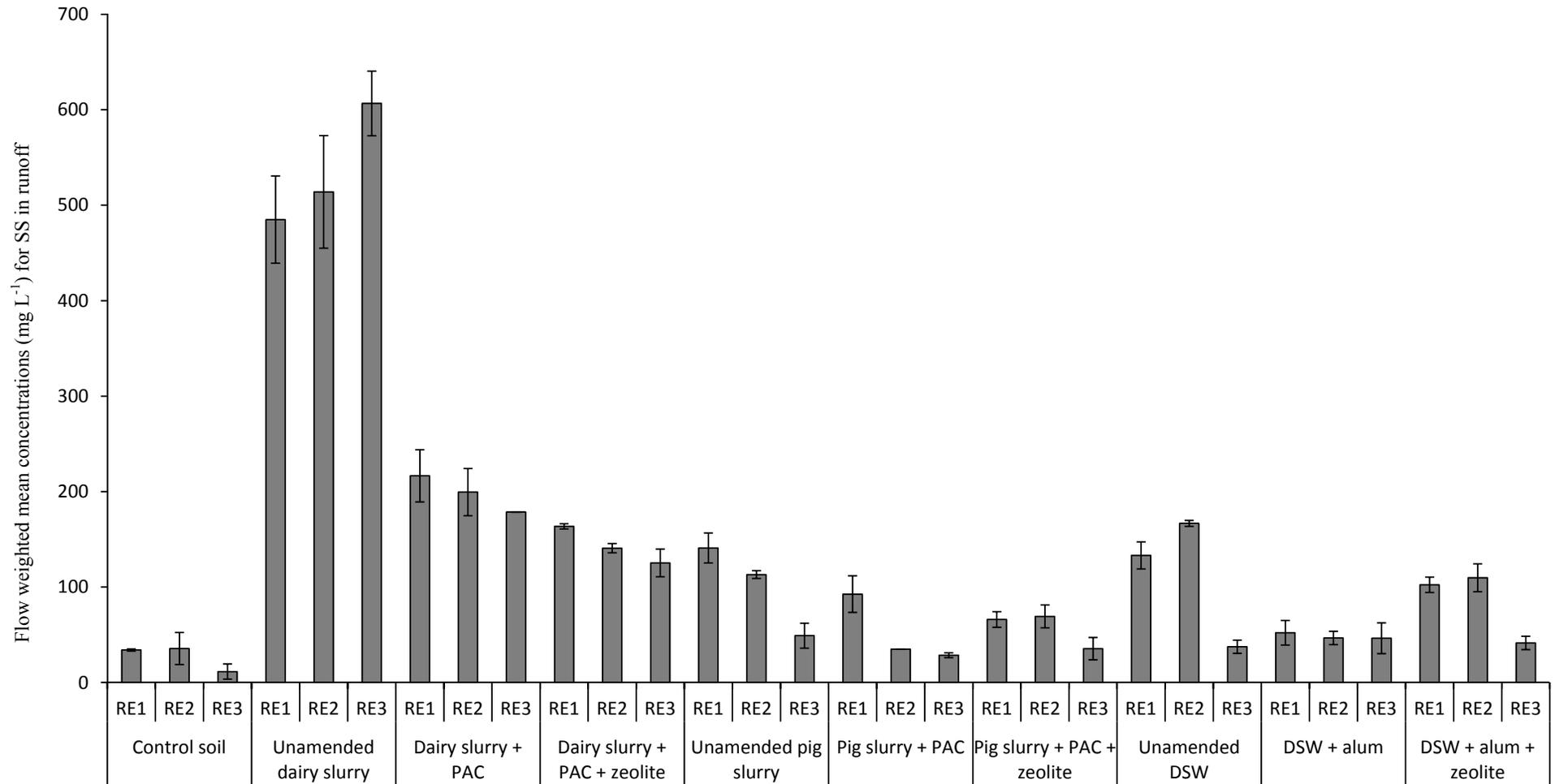


Figure 3: Histogram of flow weighted mean concentrations for SS in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h.

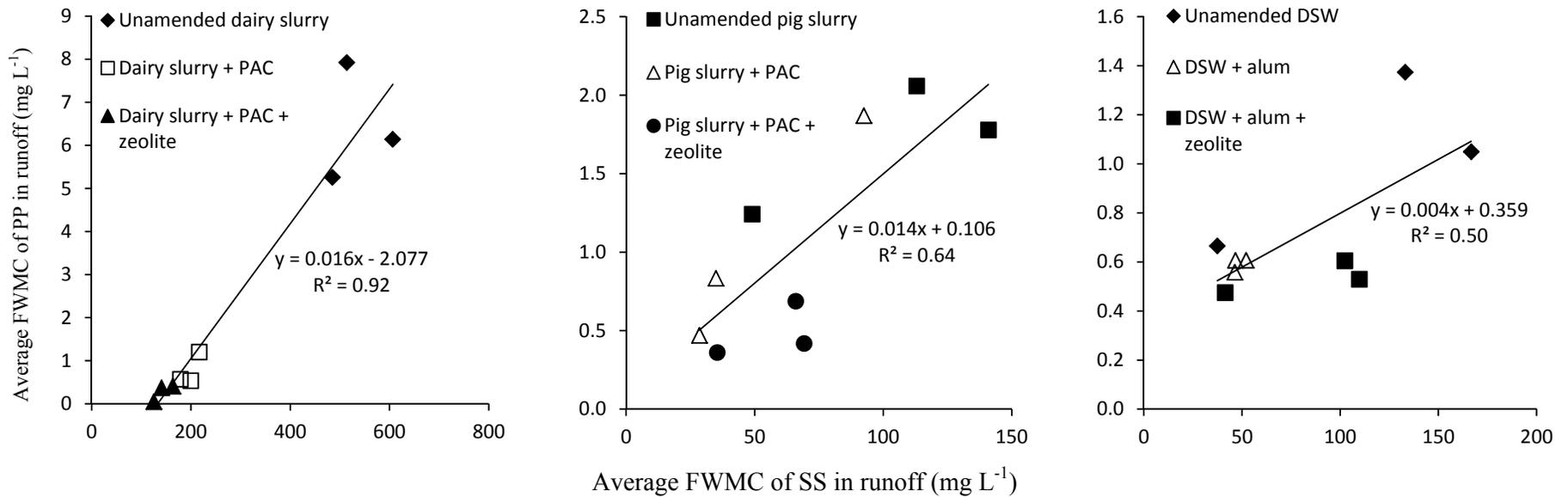


Figure 4: Correlation between suspended solid (SS) concentrations and corresponding particulate phosphorus (PP) concentrations for dairy slurry, pig slurry and DSW averaged over all three rainfall events. The data includes unamended wastes, wastes amended with PAC/alum only (no zeolite) and combined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