



## **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**

Title	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
Author(s)	Murnane, J. G.; Brennan, R. B.; Fenton, O.; Healy, Mark G.
Publication Date	2015-09-16
Publisher	Crop Science Society of America
Repository DOI	<a href="https://doi.org/10.2134/jeq2014.07.0319">10.2134/jeq2014.07.0319</a>

1 **Published as: Murnane, J.G., Brennan, R.B., Fenton, O., Healy, M.G. 2016.**  
2 **Zeolite combined with alum and aluminium chloride mixed with agricultural**  
3 **slurries reduces carbon losses in runoff from grassed soil boxes. Journal of**  
4 **Environmental Quality 44(5): 1674 – 1683. doi: 10.2134/jeq2014.07.0319**

5  
6  
7 **Zeolite combined with alum and polyaluminum chloride (PAC) mixed with**  
8 **agricultural slurries reduces carbon losses in runoff from grassed soil boxes**

9 J.G. Murnane<sup>1,2</sup>, R.B. Brennan<sup>1</sup>, M.G. Healy<sup>1\*</sup>, O. Fenton<sup>3</sup>

10 <sup>1</sup>Civil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of  
11 Ireland.

12 <sup>2</sup>Civil Engineering and Materials Science, University of Limerick, Co. Limerick, Rep.  
13 of Ireland.

14 <sup>3</sup>Teagasc, Johnstown Castle, Environment Research Centre, Co Wexford, Rep. of  
15 Ireland

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

18

19 **Abbreviation list:**

20 DOC – dissolved organic carbon

21 DM – dry matter

22 FWMC – flow-weighted mean concentration

23 MWW – milk house wash water

24 PAC – polyaluminum chloride

25 SOC – soil organic carbon

26 SS – suspended solids

27 TIC – total inorganic carbon

28 TOC – total organic carbon

29

30 **Core Ideas**

31 • Slurry application to land may increase carbon concentration in surface runoff.

32 • PAC, alum and zeolite were used to mitigate carbon losses in surface runoff.

33 • Dual application of zeolite and chemical amendments reduced TOC losses.

34 • Use of amendments may not be economically viable to reduce TOC losses.

35

36 **Abstract**

37 Carbon (C) losses from agricultural soils to surface waters can migrate through water  
38 treatment plants and result in the formation of disinfection by-products (DBP), which  
39 are potentially harmful to human health. This study aimed to (1) quantify total organic  
40 carbon (TOC) and total inorganic carbon (TIC) losses in runoff after application of  
41 either dairy slurry, pig slurry, or milk house wash water (MWW) to land, and (2)  
42 mitigate these losses through co-amendment of the slurries with zeolite (2.36 – 3.35  
43 mm clinoptilolite) and either liquid polyaluminum chloride (PAC) (10% Al<sub>2</sub>O<sub>3</sub>) for  
44 dairy and pig slurries or liquid aluminum sulfate (alum) (8% Al<sub>2</sub>O<sub>3</sub>) for MWW. Four  
45 treatments under repeated 30 min simulated rainfall events (9.6 mm h<sup>-1</sup>) were  
46 examined in a laboratory study using grassed soil runoff boxes (0.225 m wide and 1 m  
47 long, 10% slope): (1) control soil (2) unamended slurries (3) PAC-amended dairy and  
48 pig slurries (13.3 and 11.7 kg t<sup>-1</sup>, respectively); alum-amended MWW (3.2 kg t<sup>-1</sup>), and  
49 (4) combined zeolite and PAC-amended dairy (160 and 13.3 kg t<sup>-1</sup> zeolite and PAC,  
50 respectively) and pig slurries (158 and 11.7 kg t<sup>-1</sup> zeolite and PAC, respectively); and

51 combined zeolite and alum-amended MWW (72 and 3.2 kg t<sup>-1</sup> zeolite and alum,  
52 respectively). The unamended and amended slurries were applied at net rates of 31, 34  
53 and 50 t ha<sup>-1</sup> for pig and dairy slurries, and MWW. Significant reductions of TOC in  
54 runoff compared to unamended slurries were measured for PAC-amended dairy and  
55 pig slurries (52% and 56%, respectively), but not for alum-amended MWW. Dual  
56 zeolite and alum-amended MWW significantly reduced TOC in runoff compared to  
57 alum amendment only. We conclude that use of PAC-amended dairy and pig slurries  
58 and dual zeolite and alum-amended MWW, while effective, may not be economically  
59 viable to reduce TOC losses from organic slurries given the relatively low amounts of  
60 TOC measured in runoff from unamended slurries compared to the amounts applied.

61

62 *Keywords:* agricultural slurries, total organic carbon, total inorganic carbon, soil  
63 organic carbon, surface runoff.

64

## 65 **1. Introduction**

66 Application of organic slurries to agricultural soils may result in increased carbon (C)  
67 and nutrient losses to ground and surface waters, increased greenhouse gas emissions,  
68 and ammonia volatilization (Jardé et al., 2007; Morel et al., 2009; Chadwick et al.,  
69 2011; Li et al., 2013; O' Flynn et al., 2013). Over the last two decades elevated levels  
70 of dissolved organic carbon (DOC) in surface waters have been observed in the UK  
71 (Freeman et al., 2001; Evans et al., 2005; Worrall and Burt, 2007), Europe (Skjelkvåle  
72 et al., 2001; Hejzlar et al., 2003), North America, and Canada (Burns et al., 2006;  
73 Zhang et al., 2010; Couture et al., 2012). These elevated levels are attributed to a  
74 variety of influences including increased air temperatures (Bellamy et al., 2005;  
75 Powlson, 2005; Toosi et al., 2014), precipitation (Hongve et al., 2004; Dalzell et al.,

76 2005; Clark et al., 2007; Raymond and Oh, 2007; Hernes et al., 2008), atmospheric  
77 influences (Monteith et al., 2007), and changes in agricultural practices including  
78 increased spreading of agricultural slurries to soils (Owens et al., 2002; Chen and  
79 Driscoll, 2009; Ostle et al., 2009; Sickman et al., 2010; Delpla et al., 2011; Oh et al.,  
80 2013).

81

82 The amount of C, and particularly soil organic carbon (SOC), in soils is the most  
83 frequently used indicator of the condition and health of a soil (e.g. Reeves 1997; Van-  
84 Camp et al., 2004; Arias et al., 2005), and recent studies have linked land use  
85 management to C losses with corresponding soil quality deterioration and reduced  
86 productivity (Cui et al., 2014; Waring et al., 2014). Soil organic C levels below a  
87 critical 2% threshold (i.e. percentage of SOC in a sample using dry combustion or  
88 elemental analysis techniques) are widely believed to negatively impact the soil  
89 structure, although quantitative evidence of this seems lacking (Loveland and Webb,  
90 2003). Blair et al. (2006) observed that small changes in total C content can have  
91 disproportionately large effects on soil structural stability. On the other hand,  
92 excessive SOC levels above which there is no agronomic benefit in terms of crop  
93 production (Zhang et al., 2016) may also adversely impact the soil structure (Haynes  
94 and Naidu, 1998), and may result in C losses to ground and surface waters.

95

96 Application of organic manures increases soil SOC to a greater extent than inorganic  
97 fertilizers (Huang et al., 2010; Gattinger et al., 2012; Li and Han, 2016), and grassed  
98 soils offer a greater potential for C storage than tilled or disturbed soils because of  
99 their greater protection of micro (<250  $\mu\text{m}$ ) and macro (>2000  $\mu\text{m}$ ) aggregate  
100 associated C (Balesdent et al., 2000; Deneff et al., 2001; Deneff et al., 2007; Zotarelli et

101 al., 2007). Therefore, undisturbed soils such as grasslands offer greater potential to  
102 mitigate atmospheric carbon dioxide (CO<sub>2</sub>), as well as nitrous oxide (N<sub>2</sub>O) emissions,  
103 and it may be environmentally beneficial to focus the application of organic slurries to  
104 grassed soils. This, however, would increase the risk of surface runoff and leaching  
105 during, or immediately after, application, and options to mitigate these risks need to  
106 be explored.

107

108 Total inorganic carbon (TIC) makes up approximately one third of global soil carbon  
109 stocks (748 Pg (1 Pg = 10<sup>15</sup> g or 1 Gt) in the upper 1 m of soil, with the remainder  
110 made up of total organic carbon (TOC) (1,548 Pg) (Batjes, 2014). Although not as  
111 agronomically important as TOC, TIC has potential for enhanced long-term  
112 sequestration of atmospheric CO<sub>2</sub>, particularly as pedogenic (i.e. formed within soil)  
113 carbonates are stable for extremely long periods of time (Manning, 2008; Rawlins et  
114 al., 2011). It is becoming increasingly important, therefore, to monitor inorganic as  
115 well as organic carbon in soils, to gain a more thorough understanding of soil carbon  
116 dynamics and its impact on the global carbon cycle.

117

118 High concentrations of TOC in surface waters have negative implications for water  
119 quality (Seekell et al., 2015; Thrane et al., 2014) and potentially human health,  
120 particularly when these waters are abstracted for potable treatment. High TOC  
121 concentrations can act as a transport mechanism for micro pollutants such as  
122 pesticides and metals (Loux, 1998; Ravichandran, 2004; Rencz et al., 2003), and can  
123 be difficult to remove by conventional water treatment (Stackelberg et al., 2004).  
124 They can also increase the potential for formation of disinfection by-products (DBP)  
125 following chlorination (Gopal et al., 2007; Hrudey, 2009). Trihalomethanes (THMs)

126 are the primary DBP of concern and are considered harmful to human health at  
127 concentrations  $>100 \mu\text{g L}^{-1}$  (Minear and Amy, 1995; U.S. EPA, 2006). Therefore,  
128 removal of TOC at the source is seen as the most effective way of reducing the risk of  
129 THM formation (Minear and Amy, 1995; Crittenden et al., 2012). To date, few  
130 studies have quantified C losses to runoff following land application of various  
131 agricultural slurries (e.g. McTiernan et al., 2001; Delpla et al., 2011), and no study has  
132 assessed the effectiveness of applying amendments to land-applied agricultural  
133 slurries to mitigate C losses in runoff to surface waters.

134

135 Therefore, the aims of this study were to quantify: (1) total carbon (including TOC  
136 and TIC) losses in runoff to surface waters following land application of three types  
137 of agricultural slurries (dairy slurry, pig slurry, and milk house wash water (MWW))  
138 and (2) the effectiveness of applying amendments to the slurries to mitigate these  
139 losses. The authors have previously investigated the effectiveness of chemical  
140 amendments (polyaluminum chloride (PAC), comprising 10%  $\text{Al}_2\text{O}_3$  applied to dairy  
141 and pig slurries; and alum, comprising  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  applied to MWW) applied  
142 alone, or in combination with zeolite to reduce nitrogen (N), phosphorus (P) and  
143 suspended solids (SS) losses from grassed soil in rainfall simulation studies (Murnane  
144 et al., 2015). The objective of the current study was to investigate if these  
145 amendments, applied at the same rates, were also effective in reducing C losses.

146

## 147 **2. Materials and Methods**

### 148 **Soil**

149 Intact grassed soil samples (45 no.), 0.5 m long, 0.3 m wide and 0.1 m deep, were cut  
150 using a spade and transported on flat timber pallets from a dry stock farm, which had

151 not received manure or fertilizer application for > 10 yr before the experiment in  
152 Galway, Republic of Ireland. The established grass (perennial ryegrass, *Lolium*  
153 *perenne* L.) length was approximately 350 - 400 mm and was cut to approximately 25  
154 mm in the laboratory runoff boxes, where it remained alive for the duration of the  
155 experiment. The soil pH ( $6.4 \pm 0.3$ ) was measured (n=3) using a pH probe and a 2:1  
156 ratio of deionized water to soil (Thomas et al., 1996). Particle size distribution was  
157 determined using a sieving and pipette method, bulk density ( $1.02 \pm 0.07$  g cm<sup>-3</sup>) using  
158 the core method (British Standard (BS) 1377-2; BSI, 1990a), and organic content  
159 ( $5 \pm 2\%$ ) by the loss of ignition test (BS 1377-3; BSI, 1990b). The soil had a sandy  
160 loam texture ( $57 \pm 5\%$  sand,  $29 \pm 4\%$  silt and  $14 \pm 2\%$  clay) and was classified as an acid  
161 brown earth Cambisol (WRB classification).

162

### 163 **Agricultural slurries**

164 Three types of agricultural slurries were collected in 25 L containers from the Teagasc  
165 Agricultural Research Centre, Moorepark, Fermoy, Co. Cork. They were (1) dairy  
166 slurry taken from a dairy cow slatted unit (2) pig slurry taken from the slurry tank of  
167 an integrated pig unit, and (3) MWW taken from a milking parlor washwater  
168 collection sump. All slurries were homogenized immediately prior to collection and  
169 were transferred directly to a temperature controlled room ( $10.4 \pm 0.7$  °C) in the  
170 laboratory. All slurry samples were tested within 24 h of collection (n=3) for TOC  
171 and TIC (Table 1) using the method of oxidation by combustion followed by infra-red  
172 measurement of CO<sub>2</sub> (BS EN 1484, 1997) using a BioTector analyzer (BioTector  
173 Analytical Systems Ltd). Total phosphorus (TP) was measured using persulfate  
174 digestion and dry matter (DM) was measured by drying at 105 °C for 24 h (APHA,  
175 2005).



176

177 **Slurry amendments**

178 The results of a laboratory study by Murnane et al. (2015) determined the optimum  
179 combined chemical and zeolite application rates for reductions in ammonium-N  
180 ( $\text{NH}_4\text{-N}$ ) and orthophosphate ( $\text{PO}_4\text{-P}$ ), and these were used in the current study. The  
181 amendments applied were (1) commercial grade liquid PAC (10%  $\text{Al}_2\text{O}_3$ ) added to the  
182 dairy and pig slurries at rates equivalent to 13.3 and 11.7  $\text{kg t}^{-1}$  (10.10 and 8.08 mg per  
183 runoff box), and commercial grade liquid aluminum sulfate (alum) (8%  $\text{Al}_2\text{O}_3$ ) added  
184 to the MWW at a rate equivalent to 3.2  $\text{kg t}^{-1}$  (3.61 mg per runoff box). Turkish zeolite  
185 (clinoptilolite), comprising 66.7%  $\text{SiO}_2$  and 10.4%  $\text{Al}_2\text{O}_3$ , was sieved to 2.36 – 3.35  
186 mm and added at rates equivalent to 160, 158, and 72  $\text{kg t}^{-1}$  (121.5, 109.4 and 81g per  
187 runoff box) to the dairy and pig slurries and MWW, respectively.

188

189 The efficacy of the zeolite and PAC/alum to also reduce TOC and TIC at the applied  
190 application rates was investigated in batch experiments ( $n = 3$ ). Varying amounts of  
191 PAC ranging from 50 to 3500  $\mu\text{L}$  were added to approximately 75 mL of dairy and  
192 pig slurries, and varying amounts of alum ranging from 50 to 1000  $\mu\text{L}$  were added to  
193 approximately 75 mL of MWW. Similarly, varying masses of graded zeolite ranging  
194 from 2 to 20 g was placed in 100 mL flasks before adding approximately 75 mL of  
195 each slurry type to the samples. All samples were shaken for 24 h at 250 excursions  
196 per minute (epm) on a reciprocating shaker and, on removal, were allowed to settle  
197 for 1 h, and the supernatant was tested for TOC and TIC using a BioTector analyzer.

198

199 **Rainfall simulation study**

200 Aluminum runoff boxes, 1 m long, 0.225 m wide and 0.05 m deep, with side walls  
201 0.025 m higher than the soil surface, were placed at a 10% slope (representative of  
202 local terrain) to the horizontal under the rainfall simulator (n=3). Each runoff box had  
203 5 mm diameter drainage holes located at 0.3 m intervals along the base, which was  
204 covered with muslin cloth to prevent soil loss. Rainfall was generated using a mains  
205 water supply (pH 7.7±0.2, electrical conductivity 0.435 dS m<sup>-1</sup>), at an intensity of 9.6  
206 ±0.16 mm h<sup>-1</sup> (representative of a 2 yr, 1 h rainfall event) and average uniformity  
207 coefficient of 0.84 over the experimental area (2.1 m × 2.1 m) using a single 1/4HH-  
208 SS14SQW nozzle (Spraying Systems Co. Wheaton, IL) placed approximately 3.4 m  
209 above the soil surface. The intact grassed soil samples were trimmed by hand (0.45–  
210 0.5 m long, 0.225 m wide and 0.05 m deep), placed firmly in the runoff boxes,  
211 saturated from the base, and then left to drain for 24 h to replicate field capacity  
212 conditions. At this point (t = 24 h), amended and unamended slurries were stirred and  
213 applied by even and consistent hand spreading in repeated figure eight patterns to the  
214 grassed soil at rates, net of applied amendments, equivalent to 31, 34 and 50 t ha<sup>-1</sup>  
215 (759, 691 and 1,125 g per runoff box) for pig and dairy slurries and MWW, and left  
216 for 48 h. The applied rates were the maximum permissible based on a limit of 19 kg P  
217 ha<sup>-1</sup> for dairy and pig slurries and a volumetric limit of 50 m<sup>3</sup> ha<sup>-1</sup> for MWW (S.I. No.  
218 31 of 2014). In addition, unamended soil boxes (n=3) were used as controls. At t = 72,  
219 96 and 120 h, successive rainfall events were applied (RE1, RE2, RE3, respectively),  
220 each lasting 30 min after continuous runoff was observed. During each rainfall  
221 simulation, the surface runoff was collected at time intervals of 10, 20 and 30 min,  
222 and TOC and TIC were measured immediately using a BioTector analyzer.  
223 Subsamples taken at 5 min intervals were thoroughly mixed and measured for SS by

224 vacuum filtration through Whatman GF/C glass fiber filters (pore size 1.2  $\mu\text{m}$ )  
225 (APHA, 2005).

226

### 227 **Data analysis**

228 Flow-weighted mean concentrations (FWMCs) were determined for each rainfall  
229 simulation event and the data were analyzed using one way ANOVA in SPSS (IBM  
230 SPSS Statistics 20 Core System) with treatment as a factor. Logarithmic  
231 transformations were required for all variables to satisfy the normal distributional  
232 assumptions. Probability values of  $p > 0.05$  were deemed not to be significant.

233

## 234 **3 Results and Discussion**

### 235 **Batch studies and amendment application rates**

236 The applied PAC/alum rates (based on N and P removals (Murnane et al., 2015)) were  
237 less than those which provided optimum TOC and TIC removals for all slurries except  
238 for MWW, where increased application of alum did not improve TOC removal rates  
239 (Fig 1). This was most likely due to the reduced opportunity for alum to coagulate the  
240 SS in the more dilute MWW ( $0.7 \pm 0.3$  % DM) when compared to the dairy ( $8.0 \pm 0.1$  %  
241 DM) and pig ( $2.6 \pm 0.1$  % DM) slurries. The batch studies also showed that a 2.3 fold  
242 increase in the PAC application (from applied volumetric ratio of 0.0111 to 0.0256)  
243 resulted in a corresponding eight fold increase in TOC removal from dairy slurry (100  
244 to 800 mg). Similarly for pig slurry, an approximate doubling of the PAC application  
245 rate (from volumetric ratio of 0.0097 to 0.0197) resulted in a corresponding  
246 approximate three-fold increase in TOC removal (170 to 500 mg) (Fig. 1). The  
247 maximum zeolite adsorption capacities for TOC and TIC (Table 2) indicate that the  
248 ability of zeolite to remove TOC might be impacted by the DM of the slurries (Table

249 1) with the highest removals from MWW (the most dilute slurry) followed by pig and  
250 dairy slurries. Therefore, the batch studies indicated that the effectiveness of  
251 PAC/alum applications to remove TOC increased with increasing slurry DM content  
252 and conversely, the effectiveness of zeolite to remove TOC decreased with increasing  
253 slurry DM content.

254

255 The TOC and TIC removal rates for PAC-amended dairy and pig slurries and alum-  
256 amended MWW were much higher than those for zeolite (Table 2). The reduction of  
257 TOC and TIC from the slurries amended with either PAC or alum was via the process  
258 of coagulation of the SS and colloidal matter (Matilainen et al., 2010; Alexander et  
259 al., 2012) which may have involved a number of removal mechanisms, including  
260 destabilization (charge neutralization), entrapment (including sweep flocculation),  
261 adsorption, and complexation with coagulant metal ions into insoluble particulate  
262 aggregates (Crittenden et al., 2012). It was observed that excessive application of  
263 PAC to the pig slurry (> volumetric ratio of 0.0197 PAC: slurry; Fig 1) resulted in a  
264 rapid decrease in the removal of TOC and TIC. This was likely due to charge reversal  
265 of the colloidal particles at high dosage rates (Black et al., 1966).

266

### 267 **Rainfall simulation study**

268 Significant ( $p < 0.001$ ) increases in FWMCs of TOC were observed for all unamended  
269 slurry applications over the three rainfall events when compared to the control soil  
270 and were highest for dairy slurry followed by pig slurry and MWW (Fig. 2). The  
271 higher TOC content of the dairy slurry compared with the pig slurry, as well as its  
272 higher application rate (34 vs. 31 t ha<sup>-1</sup>), was a contributing factor to the higher  
273 FWMC in runoff. Total organic carbon concentrations were reduced compared to the

274 unamended slurries ( $p < 0.001$ ) following application of PAC-amended dairy and pig  
275 slurries, but the reductions for alum-amended MWW were not significant (Figure 2,  
276 Table 3). Significant ( $p < 0.05$ ) reductions in TOC were measured for MWW amended  
277 with zeolite and alum when compared to alum amendments only and for dairy slurry  
278 amended with zeolite and PAC when compared to PAC amendments only. However,  
279 pig slurry amended with zeolite and PAC, was not significantly lower than that  
280 amended with PAC only. Average reductions in FWMCs of TIC in runoff compared  
281 to unamended slurries over the three rainfall events were significant only for pig  
282 slurry ( $p < 0.001$ ) (increases in TIC were observed for dairy slurry and MWW);  
283 however, average TIC concentrations remained below those of the control soil for all  
284 slurries and all treatments (Table 3).

285

#### 286 **Relationship between suspended solids and carbon losses in runoff**

287 The average FWMC of TOC in runoff was positively correlated with corresponding  
288 SS concentrations (Murnane et al. (2015) and Fig 3) for both unamended and  
289 amended dairy and pig slurries ( $R^2 = 0.78$  and  $0.48$ , respectively), but was not  
290 correlated with MWW (Fig. 3). In contrast, there was a negative correlation between  
291 SS concentrations and average FWMC of TIC in runoff for dairy slurry, a weak  
292 positive correlation for pig slurry ( $R^2 = 0.31$ ), and a negative correlation for MWW  
293 (Fig. 3). Chemical amendments flocculate slurry particles, which once entrained on  
294 the soil surface, have a high resistance to being washed off during repeated rainfall  
295 events (McCalla, 1944; Kang et al., 2014). Particulate organic matter in land-applied  
296 slurries contain colloidal particles, which have a large specific surface area and  
297 provide the greatest number of sites for sorption of pollutants, including carbon. In a  
298 particle size fractionation study of pig slurry, Aust et al. (2009) found that particle

299 size fractions <63  $\mu\text{m}$  contained 50% of slurry DM, and it is these sized colloidal  
300 particles that are usually released in surface runoff following land application of  
301 agricultural manures immediately after the start of a rainfall event or in high intensity  
302 storms (Delpla et al., 2011). Studies to measure the enrichment ratios (ER) (ratio of C  
303 concentration in eroded sediment to the original concentration of sediment from  
304 where the eroded sediment originated) of C in runoff (Jin et al., 2008; Jacinthe et al.,  
305 2004) have reported ERs ranging from 1.01 to 3.4, while ERs between 1.16 – 2.33 in  
306 particles mobilized by rainfall splash under natural precipitation have also been  
307 measured (Beguería et al., 2015). Polyaluminum chloride was most effective at  
308 removing TOC (even though the applied rate was less than the optimum (Fig. 1)) and  
309 SS from dairy slurry, which had the highest DM content (8%). In contrast, alum was  
310 least effective at removing TOC from MWW, which had the lowest DM (0.7%). This  
311 indicated that PAC had a greater opportunity to coagulate the C-enriched colloidal  
312 particles in the dairy slurry but was less able to coagulate the pig slurry (2.6% DM),  
313 as less of it remained on top of the soil during the rainfall events. Similarly, alum was  
314 least able to coagulate the dilute MWW, and was therefore least effective in  
315 mitigating TOC losses. Application of combined zeolite and alum amendments  
316 significantly ( $p < 0.05$ ) reduced TOC in runoff from MWW when compared with alum  
317 amendments only (Table 3, Fig. 2). This indicates that zeolite has a role in C  
318 sequestration in runoff, particularly from slurries with a low DM content, and  
319 corroborates the results of the zeolite adsorption tests carried out in the batch studies  
320 (Table 2).

321

322 **Implications for use of amendments at field-scale**

323 In this study, the use of dual zeolite and PAC/alum amendments with land applied  
324 organic slurries have been shown to be reasonably effective in retaining a proportion  
325 of the TOC lost in runoff (range 51-76%, Table 3) under simulated rainfall even  
326 though the PAC/alum was not applied at optimum TOC removal rates (Fig. 1).  
327 However, in a wider context, the amounts of TOC lost in surface runoff from the  
328 unamended slurries as a proportion of the amounts applied were quite low (2.2, 3.1  
329 and 17.4% from dairy and pig slurries and MWW, respectively) and these losses were  
330 reduced for all slurries following application of either PAC/alum amendments or dual  
331 amendments of zeolite and either PAC/alum, with highest removal rate of 8.9% (from  
332 17.4% to 8.5%) for MWW (Table 4). The estimated costs per m<sup>3</sup> of applying the  
333 amendments (in Ireland) for dairy and pig slurries, and MWW, respectively, are €190,  
334 €188 and €84 for dual zeolite and either PAC or alum, and €6.40, €5.60 and €0.80 for  
335 PAC/alum amendments only (Murnane et al., 2015). While it is recognized that these  
336 costs will vary regionally, it is clear that the economic benefits of carbon  
337 sequestration by application of dual zeolite and PAC/alum amendments may be  
338 prohibitive for all slurries. The benefits of applying PAC only to the dairy and pig  
339 slurries and alum to the MWW for carbon removal may also be uneconomical at the  
340 rates indicated.

341

### 342 **3 Conclusions**

343 Dual application of zeolite and either PAC to dairy and pig slurries or alum to MWW  
344 reduced TOC in runoff from grassed soil runoff boxes under repeated simulated  
345 rainfall. Increases in TOC in runoff were measured following application of  
346 unamended slurries when compared to the control soil. Significant ( $p < 0.001$ )  
347 reductions of TOC in runoff were observed by the use of PAC amendments for dairy

348 and pig slurries and by use of dual zeolite and alum amendments to MWW.  
349 Reductions in TIC were significant only for PAC amended pig slurry ( $p < 0.001$ ) but  
350 remained below those of the control soil for all slurries and all treatments. Total  
351 organic carbon losses were correlated to SS concentrations in runoff, and indicated  
352 that the C removal mechanisms depend on the DM content of the slurry. Given the  
353 relatively low amounts of TOC measured in runoff from unamended slurries  
354 compared to the amounts applied, widespread application of amendments may not be  
355 economically viable at field-scale to reduce TOC losses.

356

### 357 **Acknowledgments**

358 The authors wish to acknowledge the assistance provided by Mary O'Brien, Dermot  
359 McDermott, Gerry Hynes and Peter Fahy during the course of the experimental work.

360



361 **References**

- 362 Alexander, J.T., F.I. Hai, and T.M. Al-aboud. 2012. Chemical coagulation-based  
363 processes for trace organic contaminant removal: Current state and future  
364 potential. *J. Environ. Manage.* 111: 195-207.
- 365 APHA. 2005. Standard methods for the examination of water and wastewater,  
366 American Public Health Association, American Water Works Association, Water  
367 Pollution Control Federation, Washington, DC.
- 368 Arias, M.E., J.A. González-Pérez, F.J. González-Vila, and A.S. Ball. 2005. Soil  
369 health—a new challenge for microbiologists and chemists. *Int. Microbiol.* 8 :13-  
370 21.
- 371 Aust, M.O., S. Thiele-Bruhn, K.U. Eckhardt, and P. Leinweber. 2009. Composition of  
372 organic matter in particle size fractionated pig slurry. *Biores. Technol.* 100:  
373 5736-5743.
- 374 Balesdent, J., C. Chenu, and M. Balabane. 2000. Relationship of soil organic matter  
375 dynamics to physical protection and tillage. *Soil Till. Res.* 53: 215-230.
- 376 Batjes, N. H. 2014. Total carbon and nitrogen in the soils of the world. *European J.*  
377 *Soil Sci.* 65: 10-21.
- 378 Beguería, S., M. Angulo-Martínez, L. Gaspar, and A. Navas. 2015. Detachment of  
379 soil organic carbon by rainfall splash: experimental assessment on three  
380 agricultural soils of Spain. *Geoderma* 245: 21-30.
- 381 Bellamy, P.H., P.J. Loveland, R.I. Bradley, R.M. Lark, and G.J. Kirk, 2005. Carbon  
382 losses from all soils across England and Wales 1978–2003. *Nature* 437: 245-248.
- 383 Black, A.P., F.B. Birkner, and J.J. Morgan. 1966. The effect of polymer adsorption on  
384 the electrokinetic stability of dilute clay suspensions. *J. Colloid Interface Sci.* 21:  
385 626-648.
- 386 Blair, N., R.D. Faulkner, A.R. Till, and P.R. Poulton. 2006. Long-term management  
387 impacts on soil C, N and physical fertility: Part I: Broadbalk experiment. *Soil*  
388 *Till. Res.* 91: 30-38.
- 389 British Standards Institution. 1990a. British standard methods of test for soils for civil  
390 engineering purposes. Determination of particle size distribution. BS  
391 1377:1990:2. BSI, London.
- 392 British Standards Institution. 1990b. Determination by mass-loss on ignition. British  
393 standard methods of test for soils for civil engineering purposes. Chemical and  
394 electro-chemical tests. BS 1377:1990:3. BSI, London.
- 395 British Standards Institution. 1997. Water analysis. Guidelines for the determination  
396 of total organic carbon (TOC) and dissolved organic carbon (DOC) BS EN  
397 1484:1997. BSI, London.
- 398 Burns, D.A., M.R. McHale, C.T. Driscoll, and K.M. Roy. 2006. Response of surface  
399 water chemistry to reduced levels of acid precipitation: comparison of trends in  
400 two regions of New York, USA. *Hydrol. Processes* 20: 1611-1627.

- 401 Chadwick, D., S.G. Sommer, R. Thorman, D. Fanguero, L. Cardenas, B. Amon, and  
 402 T. Misselbrook. 2011. Manure management: implications for greenhouse gas  
 403 emissions. *Animal Feed Sci. Technol.* 166: 514-531.
- 404 Chen, X., and C.T. Driscoll. 2009. Watershed land use controls on chemical inputs to  
 405 Lake Ontario embayments. *J. Environ. Qual.* 38: 2084-2095.
- 406 Clark, J.M., S.N. Lane, P.J. Chapman, and J.K. Adamson. 2007. Export of dissolved  
 407 organic carbon from an upland peatland during storm events: implications for  
 408 flux estimates. *J. Hydrol.* 347: 438-447.
- 409 Couture, S., D. Houle, and C. Gagnon. 2012. Increases of dissolved organic carbon in  
 410 temperate and boreal lakes in Quebec, Canada. *Environ. Sci. Pollut. Res.* 19:  
 411 361-371.
- 412 Crittenden, J.C., R. Rhodes Trussell, D.W. Hand, K.J. Howe, and G. Tchobanoglous.  
 413 2012. *MWH's Water Treatment: Principles and Design.* John Wiley & Sons.
- 414 Cui, J., M. Sadegh Askari, and N.M. Holden. 2014. Relating Soil Carbon and Soil  
 415 Structure to Land Use Management. In *Soil Carbon*, pp. 297-304. Springer  
 416 International Publishing.
- 417 Dalzell, B.J., T.R. Filley, and J.M. Harbor. 2005. Flood pulse influences on terrestrial  
 418 organic matter export from an agricultural watershed. *Journal of Geophysical*  
 419 *Research: Biogeosciences* 110, no. G2.
- 420 Delpla, I., E. Baurès, A.-V. Jung, and O. Thomas. 2011. Impacts of rainfall events on  
 421 runoff water quality in an agricultural environment in temperate areas. *Sci. Tot.*  
 422 *Environ.* 409: 1683-1688.
- 423 Deneff, K., J. Six, K. Paustian, and R. Merckx. 2001. Importance of macroaggregate  
 424 dynamics in controlling soil carbon stabilization: short-term effects of physical  
 425 disturbance induced by dry-wet cycles. *Soil Biol. Biochem.* 33: 2145-2153.
- 426 Deneff, K., L. Zotarelli, R.M. Boddey, and J. Six. 2007. Microaggregate-associated  
 427 carbon as a diagnostic fraction for management-induced changes in soil organic  
 428 carbon in two Oxisols. *Soil Biol. Biochem.* 39: 1165-1172.
- 429 Evans, C.D., D.T. Monteith, and D.M. Cooper. 2005. Long-term increases in surface  
 430 water dissolved organic carbon: observations, possible causes and environmental  
 431 impacts. *Environ. Pollut.* 137: 55-71.
- 432 Freeman, C., C.D. Evans, D.T. Monteith, B. Reynolds, and N. Fenner. 2001. Export  
 433 of organic carbon from peat soils. *Nature* 412: 785-785.
- 434 Gattinger, A., A. Muller, M. Haeni, C. Skinner, A. Fliessbach, N. Buchmann, P.  
 435 Mäder, M. Stolze, P. Smith, N. El-Hage Scialabba, and U. Niggli. 2012.  
 436 Enhanced top soil carbon stocks under organic farming. *Proceed. Nat. Acad. Sci.*  
 437 109: 18226-18231.
- 438 Gopal, K., S. Swarupa Tripathy, J.L. Bersillon, and S. Prabha Dubey. 2007.  
 439 Chlorination byproducts, their toxicodynamics and removal from drinking water.  
 440 *J. Hazard. Mat.* 140: 1-6.

- 441 Haynes, R. J., and R. Naidu. 1998. Influence of lime, fertilizer and manure  
442 applications on soil organic matter content and soil physical conditions: a review.  
443 *Nutr. Cycl. Agroecosyst.* 51: 123-137.
- 444 Hejzlar, J., M. Dubrovský, J. Buchtele, and M. Růžička. 2003. The apparent and  
445 potential effects of climate change on the inferred concentration of dissolved  
446 organic matter in a temperate stream (the Malše River, South Bohemia). *Sci. Tot.*  
447 *Environ.* 310: 143-152.
- 448 Hernes, P.J., R.G.M. Spencer, R.Y. Dyda, B.A. Pellerin, P.A.M. Bachand, and B.A.  
449 Bergamaschi. 2008. The role of hydrologic regimes on dissolved organic carbon  
450 composition in an agricultural watershed. *Geochim. Cosmochim. Ac.* 72: 5266-  
451 5277.
- 452 Hongve, D., G. Riise, and J.F. Kristiansen. 2004. Increased colour and organic acid  
453 concentrations in Norwegian forest lakes and drinking water—a result of  
454 increased precipitation? *Aquat. Sci.* 66: 231-238.
- 455 Hrudey, S.E. 2009. Chlorination disinfection by-products, public health risk tradeoffs  
456 and me. *Wat. Res.* 43: 2057-2092.
- 457 Huang, S., X. Peng, Q. Huang, and W. Zhang. 2010. Soil aggregation and organic  
458 carbon fractions affected by long-term fertilization in a red soil of subtropical  
459 China. *Geoderma* 154: 364-369.
- 460 Jacinthe, P.-A., R. Lal, L. B. Owens, and D.L. Hothem. 2004. Transport of labile  
461 carbon in runoff as affected by land use and rainfall characteristics. *Soil Till.*  
462 *Res.* 77: 111-123.
- 463 Jardé, E., Gruau, G. and L. Mansuy-Huault, 2007. Detection of manure-derived  
464 organic compounds in rivers draining agricultural areas of intensive manure  
465 spreading. *Appl. Geochem.* 22:1814-1824.
- 466 Jin, K., W.M. Cornelis, W. Schiette, J. J. Lu, T. Buysse, G. Baert, H. J. Wu, Y. Yao,  
467 D.X. Cai. J.Y. Jin, S. De Neve, R. Hartmann and D. Gabriels. 2008.  
468 Redistribution and loss of soil organic carbon by overland flow under various  
469 soil management practices on the Chinese Loess Plateau. *Soil Use Manage.* 24:  
470 181-191.
- 471 Kang, J., S.E. King, R.A. McLaughlin, and J.D. Wiseman. 2014. Flocculated  
472 sediment and runoff quality improvement by polyacrylamide. *Transactions of the*  
473 *ASABE* 57: 861-867.
- 474 Li, L.-J., M.-Y. You, H.-A. Shi, X.-L. Ding, Y.-F. Qiao, and X.-Z. Han. 2013. Soil  
475 CO<sub>2</sub> emissions from a cultivated Mollisol: Effects of organic amendments, soil  
476 temperature, and moisture. *Europe. J. Soil B.* 55: 83-90.
- 477 Li, L.-J., and X.-Z. Han. 2016. Changes of soil properties and carbon fractions after  
478 long-term application of organic amendments in Mollisols. *Catena* 143: 140-144.
- 479 Loux, N.T. 1998. An assessment of mercury-species-dependent binding with natural  
480 organic carbon. *Chemical Speciation Bioavail.* 10: 127-136.
- 481 Loveland, P., and J. Webb. 2003. Is there a critical level of organic matter in the

- 482 agricultural soils of temperate regions: a review. *Soil Till. Res.* 70: 1-18.
- 483 Manning, D. A. C. 2008. Biological enhancement of soil carbonate precipitation:  
484 passive removal of atmospheric CO<sub>2</sub>. *Mineral. Mag.* 72: 639-649.
- 485 Matilainen, A., M. Vepsäläinen, and M. Sillanpää. 2010. Natural organic matter  
486 removal by coagulation during drinking water treatment: A review. *Adv. Colloid*  
487 *Interface. Sci.* 159: 189-197.
- 488 McCalla, T. M. 1944. Water-drop method of determining stability of soil structure.  
489 *Soil Sci.* 58: 117-122.
- 490 McTiernan, K.B., S.C. Jarvis, D. Scholefield, and M.H.B. Hayes. 2001. Dissolved  
491 organic carbon losses from grazed grasslands under different management  
492 regimes. *Wat. Res.* 35: 2565-2569.
- 493 Minear, R.A., and G. Amy. 1995. *Disinfection By-Products in Water Treatment The*  
494 *Chemistry of Their Formation and Control.* CRC Press.
- 495 Monteith, D.T., J.L. Stoddard, C.D. Evans, H.A. de Wit, M. Forsius, T. Høgåsen, A.  
496 Wilander, B.L. Skjelkvåle, D.S. Jeffries, J. Vuorenmaa, B. Keller, J. Kopáček,  
497 and J. Vesely. 2007. Dissolved organic carbon trends resulting from changes in  
498 atmospheric deposition chemistry. *Nature* 450: 537-540.
- 499 Murnane, J.G., R.B. Brennan, M.G. Healy, and O. Fenton. 2015. Use of zeolite with  
500 alum and polyaluminum chloride amendments to mitigate runoff losses of  
501 phosphorus, nitrogen, and suspended solids from agricultural wastes applied to  
502 grassed soils. *J. Environ. Qual.* 44: 1674-1683.
- 503 Morel, B., P. Durand, A. Jaffrezie, G. Gruau, and J. Molénat. 2009. Sources of  
504 dissolved organic carbon during stormflow in a headwater agricultural  
505 catchment. *Hydrological Processes* 23: 2888-2901.
- 506 O' Flynn, C.J., M.G. Healy, P. Wilson, N.J. Hoekstra, S.M. Troy, and O. Fenton.  
507 2013. Chemical amendment of pig slurry: control of runoff related risks due to  
508 episodic rainfall events up to 48 h after application. *Environ. Sci. Pollut. Res.* 20:  
509 6019 – 6027.
- 510 Oh, N.-H., B.A. Pellerin, P.A.M. Bachand, P.J. Hernes, S.M. Bachand, N. Ohara, M.  
511 Levent Kavvas, B.A. Bergamaschi, and W.R. Horwath. 2013. The role of  
512 irrigation runoff and winter rainfall on dissolved organic carbon loads in an  
513 agricultural watershed. *Agr. Ecosyst. Environ.* 179: 1-10.
- 514 Ostle, N. J., P. E. Levy, C. D. Evans, and P. Smith. 2009. UK land use and soil carbon  
515 sequestration. *Land Use Policy* 26: S274-S283.
- 516 Owens, L. B., R. W. Malone, D. L. Hothem, G. C. Starr, and R. Lal. 2002. Sediment  
517 carbon concentration and transport from small watersheds under various  
518 conservation tillage practices. *Soil Till. Res.* 67: 65-73.
- 519 Powelson, D. 2005. Climatology: Will soil amplify climate change? *Nature* 433: 204-  
520 205.
- 521 Ravichandran, M. 2004. Interactions between mercury and dissolved organic matter -

- 522 a review. *Chemosphere* 55: 319-331.
- 523 Rawlins, B. G., P. Henrys, N. Breward, D. A. Robinson, A. M. Keith, and M. Garcia-  
524 Bajo. 2011. The importance of inorganic carbon in soil carbon databases and  
525 stock estimates: a case study from England. *Soil Use and Manage.* 27: 312-320.
- 526 Raymond, P.A., and N.-Hwan Oh. 2007. An empirical study of climatic controls on  
527 riverine C export from three major US watersheds. *Global Biogeochem. Cy.* 21,  
528 GB2022, doi: 10.1029/2006GB002783.
- 529 Reeves, D. W. 1997. The role of soil organic matter in maintaining soil quality in  
530 continuous cropping systems. *Soil Till. Res.* 43: 131-167.
- 531 Rencz, A. N., N. J. O'Driscoll, G. E. M. Hall, T. Peron, K. Telmer, and N. M.  
532 Burgess. 2003. Spatial variation and correlations of mercury levels in the  
533 terrestrial and aquatic components of a wetland dominated ecosystem:  
534 Kejimikujik Park, Nova Scotia, Canada. *Wat. Air Soil Pollut.* 143: 271-288.
- 535 Seekell, D.A., J.-F. Lapierre, J. Ask, A.-K. Bergström, A. Deininger, P. Rodríguez,  
536 and J. Karlsson. 2015. The influence of dissolved organic carbon on primary  
537 production in northern lakes. *Limnol. Oceanogr.* 60: 1276-1285.
- 538 SI No. 31 of 2014. European Union (Good agricultural practice for protection of  
539 waters) Regulations 2014.  
540 <https://www.agriculture.gov.ie/media/migration/ruralenvironment/environment/nitrates/SI31of2014290114.pdf>  
541
- 542 Sickman, J.O., C.L. DiGiorgio, M.L. Davisson, D.M. Lucero, and B. Bergamaschi.  
543 2010. Identifying sources of dissolved organic carbon in agriculturally  
544 dominated rivers using radiocarbon age dating: Sacramento–San Joaquin River  
545 Basin, California. *Biogeochem.* 99: 79-96.
- 546 Skjelkvåle, B. L., J. Mannio, A. Wilander, and T. Andersen. 2001. Recovery from  
547 acidification of lakes in Finland, Norway and Sweden 1990 - 1999. *Hydrology  
548 and Earth System Sciences Discussions, European Geosciences Union* 5: 327-  
549 338.
- 550 Stackelberg, P.E., E.T. Furlong, M.T. Meyer, S.D. Zaugg, A.K. Henderson, and D.B.  
551 Reissman. 2004. Persistence of pharmaceutical compounds and other organic  
552 wastewater contaminants in a conventional drinking-water-treatment plant. *Sci.  
553 Tot. Environ.* 329: 99-113.
- 554 Thomas, G. W., D. L. Sparks, A. L. Page, P. A. Helmke, R. H. Loeppert, P. N.  
555 Soltanpour, M. A. Tabatabai, C. T. Johnston, and M. E. Sumner. 1996. Soil pH  
556 and soil acidity. *Methods of soil analysis. Part 3-chemical methods*, pp 475-490.
- 557 Thrane, J.-E., D.O. Hessen, and T. Andersen. 2014. The absorption of light in lakes:  
558 negative impact of dissolved organic carbon on primary productivity. *Ecosyst.*  
559 17: 1040-1052.
- 560 Toosi, E.R., J.P. Schmidt, and M.J. Castellano. 2014. Soil temperature is an important  
561 regulatory control on dissolved organic carbon supply and uptake of soil solution  
562 nitrate. *Europe. J. Soil Biol.* 61: 68-71.

563 United States Environmental Protection Agency. 2006. National Primary Drinking  
564 Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule:  
565 Final Rule. Federal Register 71: 388-493.

566 Van-Camp, L., B. Bujarrabal, A.R. Gentile, R.J.A. Jones, L. Montanarella, C.  
567 Olazabal, and S.-K. Selvaradjou. 2004. Reports of the technical working groups  
568 established under the Thematic Strategy for Soil Protection. EUR 21319 EN/4,  
569 872 pp. Office for Official Publications of the European Communities,  
570 Luxembourg.

571 Waring, C., U. Stockmann, B.P. Malone, B. Whelan, and A.B. McBratney. 2014. Is  
572 Percent 'Projected Natural Vegetation Soil Carbon' a useful Indicator of Soil  
573 Condition? In *Soil Carbon*, pp. 219-227. Springer International Publishing.

574 Worrall, F., and T. P. Burt. 2007. Trends in DOC concentration in Great Britain. *J.*  
575 *Hydrol.* 346: 81-92.

576 Zhang, J., J. Hudson, R. Neal, J. Sereda, T. Clair, M. Turner, D. Jeffries, P. Dillon, L.  
577 Molot, K. Somers, and R. Hesslein. 2010. Long-term patterns of dissolved  
578 organic carbon in lakes across eastern Canada: Evidence of a pronounced climate  
579 effect. *Limnol. Oceanogr.* 55: 30-42.

580 Zhang, X., N.Sun, L. Wu, M. Xu, I.J. Bingham, and Z. Li. 2016. Effects of enhancing  
581 soil organic carbon sequestration in the topsoil by fertilization on crop  
582 productivity and stability: Evidence from long-term experiments with wheat-  
583 maize cropping systems in China. *Sci. Tot. Environ.* 562: 247-259.

584 Zotarelli, L., B. J. R. Alves, S. Urquiaga, R. M. Boddey, and J. Six. 2007. Impact of  
585 tillage and crop rotation on light fraction and intra-aggregate soil organic matter  
586 in two Oxisols. *Soil Till. Res.* 95: 196-206.

587  
588  
589  
590  
591  
592  
593  
594  
595  
596  
597  
598  
599  
600  
601  
602  
603  
604  
605  
606  
607

608 **List of Figures**

609 **Figure 1:** Total organic carbon (TOC) and total inorganic carbon (TIC) removals in  
610 batch study tests (n=3) following application of polyaluminum chloride (PAC) to dairy  
611 and pig slurries and alum to milk house wash water (MWW). Optimum volumetric  
612 ratios for TOC and TIC removals were 0.0256 and 0.0197 PAC:slurry for dairy  
613 and pig slurries respectively, and 0.0056 alum:slurry for MWW. Applied volumetric  
614 ratios for TOC and TIC removals were 0.0111 and 0.0097 PAC:slurry for dairy and  
615 pig slurries, respectively, and 0.0024 alum:slurry for MWW.

616 **Figure 2:** Histogram of flow weighted mean concentrations (FWMC) (n=3) for (A)  
617 total organic carbon (TOC) and (B) total inorganic carbon (TIC) in runoff from  
618 rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3  
619 (RE3) at t = 120 h. Error bars indicate standard deviation.

620 **Figure 3:** Correlation between suspended solid (SS) concentrations and  
621 corresponding total organic carbon (TOC) and total inorganic carbon (TIC)  
622 concentrations (n=3) for dairy slurry, pig slurry and milk house wash water (MWW)  
623 averaged over all three rainfall events. The data includes unamended wastes, wastes  
624 amended with PAC/alum only (no zeolite) and combined zeolite and PAC/alum  
625 amendments. Lines represent a least squares correlation analysis with correlation  
626 coefficients ( $R^2$ ) and significance (p) indicated.

627

628

629

630 **List of Tables**

631

632 **Table 1** Slurry characterization for total organic carbon (TOC), total inorganic carbon  
633 (TIC), total phosphorus (TP) and dry matter (DM) (mean  $\pm$  standard deviation) (n=3).

634

635 **Table 2** Maximum removal rates of total organic carbon (TOC) and total inorganic  
636 carbon (TIC) from dairy and pig slurries, and milk house wash water (MWW) using  
637 (1) natural zeolite (clinoptilolite) sieved to a particle size of 2.36-3.35 mm, and (2)  
638 polyaluminum chloride (PAC) for dairy and pig slurries and alum for MWW. All tests  
639 were carried out in batch studies (n=3). The zeolite adsorption data was modelled  
640 using a Langmuir adsorption isotherm. The specific gravities of PAC and alum were  
641 1.2 and 1.32, respectively.

642

643 **Table 3** Flow weighted mean concentrations in runoff (n=3) averaged over three  
644 rainfall events and % reductions (+) or increases (-) from unamended slurries for total  
645 organic carbon (TOC) and total inorganic carbon (TIC). Shaded cells mean that no  
646 values apply.

647

648 **Table 4** Mass balance of total organic carbon (TOC) in runoff boxes during simulated  
649 rainfall for (a) unamended slurries, (b) slurries amended with either polyaluminum  
650 chloride (PAC) or alum, and (c) slurries amended with zeolite and either  
651 polyaluminum chloride (PAC) or alum (dual amended slurries). The flow weighted  
652 mean concentrations in runoff (n=3) are averaged over three rainfall events and the  
653 amendment application rates are as described in Table 3.

654



**Table 1** Slurry characterization for total organic carbon (TOC), total inorganic carbon (TIC), total phosphorus (TP) and dry matter (DM) (mean  $\pm$  standard deviation) (n=3).

Slurry Type	TOC	TIC	TP	DM
	----- (mg L <sup>-1</sup> ) -----			%
Dairy slurry	15,723 $\pm$ 409	1,224 $\pm$ 33	563 $\pm$ 55	8.0 $\pm$ 0.1
Pig slurry	10,471 $\pm$ 640	392 $\pm$ 47	619 $\pm$ 30	2.6 $\pm$ 0.1
Milk house wash water	1,137 $\pm$ 75	54 $\pm$ 5	52 $\pm$ 11	0.7 $\pm$ 0.3

**Table 2** Maximum removal rates of total organic carbon (TOC) and total inorganic carbon (TIC) from dairy and pig slurries, and milk house wash water (MWW) using (1) natural zeolite (clinoptilolite) sieved to a particle size of 2.36-3.35 mm, and (2) polyaluminum chloride (PAC) for dairy and pig slurries and alum for MWW. All tests were carried out in batch studies (n=3). The zeolite adsorption data was modelled using a Langmuir adsorption isotherm. The specific gravities of PAC and alum were 1.2 and 1.32, respectively.

Slurry type	Maximum zeolite removal rates				Maximum PAC/alum removal rates		
	(1) Maximum adsorption (mg kg <sup>-1</sup> )		Correlation coefficient		Chemical added	(2) Maximum removal (mg kg <sup>-1</sup> )	
	TOC	TIC	TOC	TIC		TOC	TIC
Dairy slurry	24	53	0.38	0.46	PAC	462,303	31,352
Pig slurry	1,020	189	0.42	0.63	PAC	303,756	14,432
Milk house wash water	1,190	3	0.68	0.73	Alum	82,240	2,194

**Table 3** Flow weighted mean concentrations in runoff (n=3) averaged over three rainfall events and % reductions (+) or increases (-) from unamended slurries for total organic carbon (TOC) and total inorganic carbon (TIC). Shaded cells mean that no values apply.

<b>Slurry application</b>	<b>TOC (mg L<sup>-1</sup>)</b>	<b>% Reduction</b>	<b>TIC (mg L<sup>-1</sup>)</b>	<b>% Reduction</b>
Control	77 <sup>a†</sup>		33 <sup>d†</sup>	
D(U)	300 <sup>d</sup>		12 <sup>c</sup>	
D(P)	144 <sup>bc</sup>	52	31 <sup>d</sup>	-163
D(Z+P)	73 <sup>a</sup>	76	21 <sup>cd</sup>	-81
P(U)	236 <sup>cd</sup>		27 <sup>d</sup>	
P(P)	104 <sup>ab</sup>	56	3 <sup>a</sup>	91
P(Z+P)	84 <sup>ab</sup>	65	3 <sup>a</sup>	88
MWW(U)	214 <sup>cd</sup>		5 <sup>ab</sup>	
MWW(A)	179 <sup>c</sup>	16	12 <sup>c</sup>	-125
MWW(Z+A)	105 <sup>ab</sup>	51	9 <sup>bc</sup>	-68

D(U) Unamended dairy slurry

D(P) Dairy slurry amended with polyaluminum chloride (PAC) at 13.3 kg t<sup>-1</sup>

D(Z+P) Dairy slurry amended with zeolite at 160 kg t<sup>-1</sup> and polyaluminum chloride (PAC) at 13.3 kg t<sup>-1</sup>

P(U) Unamended pig slurry

P(P) Pig slurry amended with polyaluminum chloride (PAC) at 11.7 kg t<sup>-1</sup>

P(Z+P) Pig slurry amended with zeolite at 158 kg t<sup>-1</sup> and polyaluminum chloride (PAC) at 11.7 kg t<sup>-1</sup>

MWW(U) Unamended milk house wash water

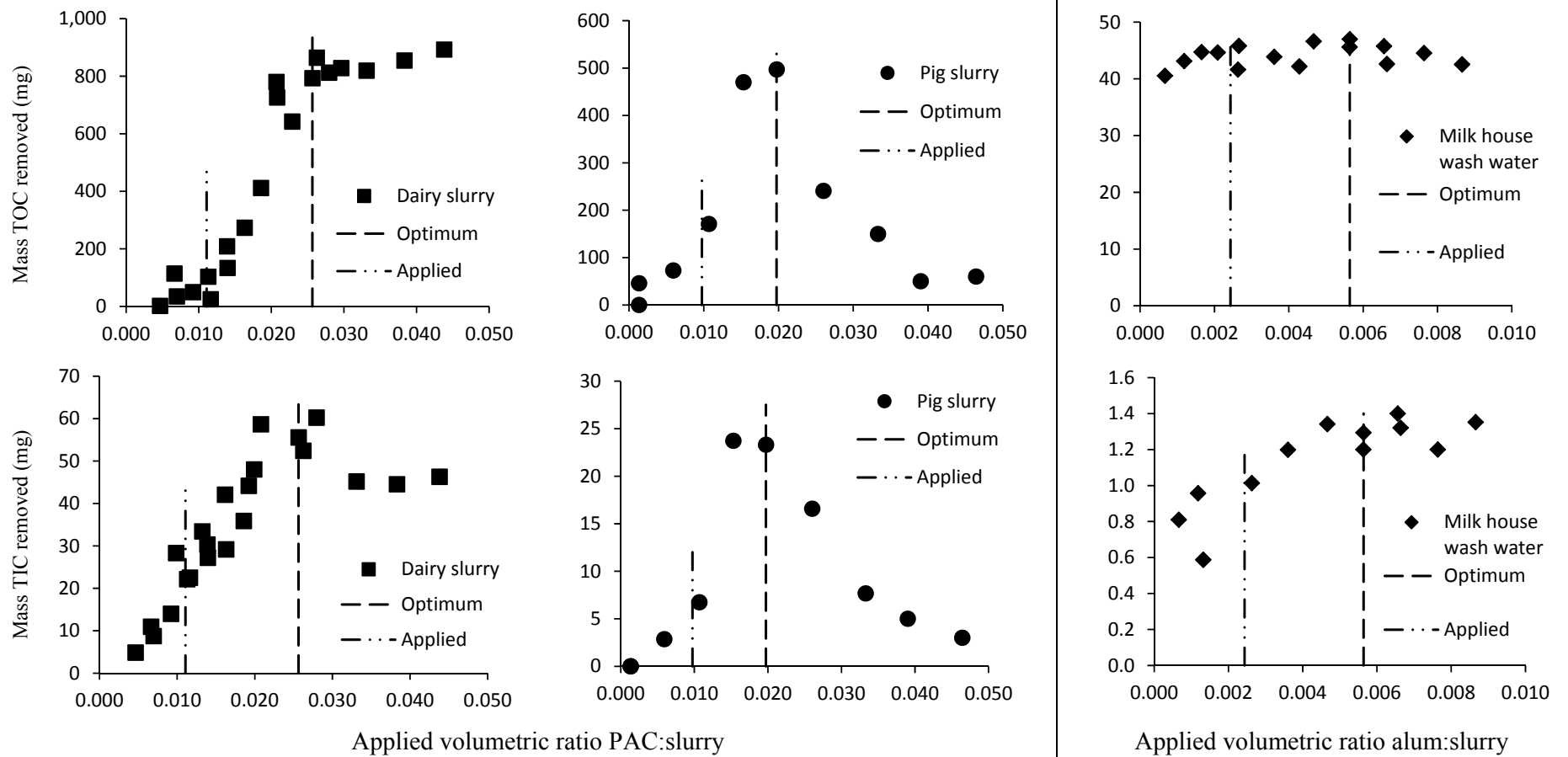
MWW(A) Milk house wash water amended with alum at 3.2 kg t<sup>-1</sup>

MWW(Z+A) Milk house wash water amended with zeolite at 72 kg t<sup>-1</sup> and alum at 3.2 kg t<sup>-1</sup>

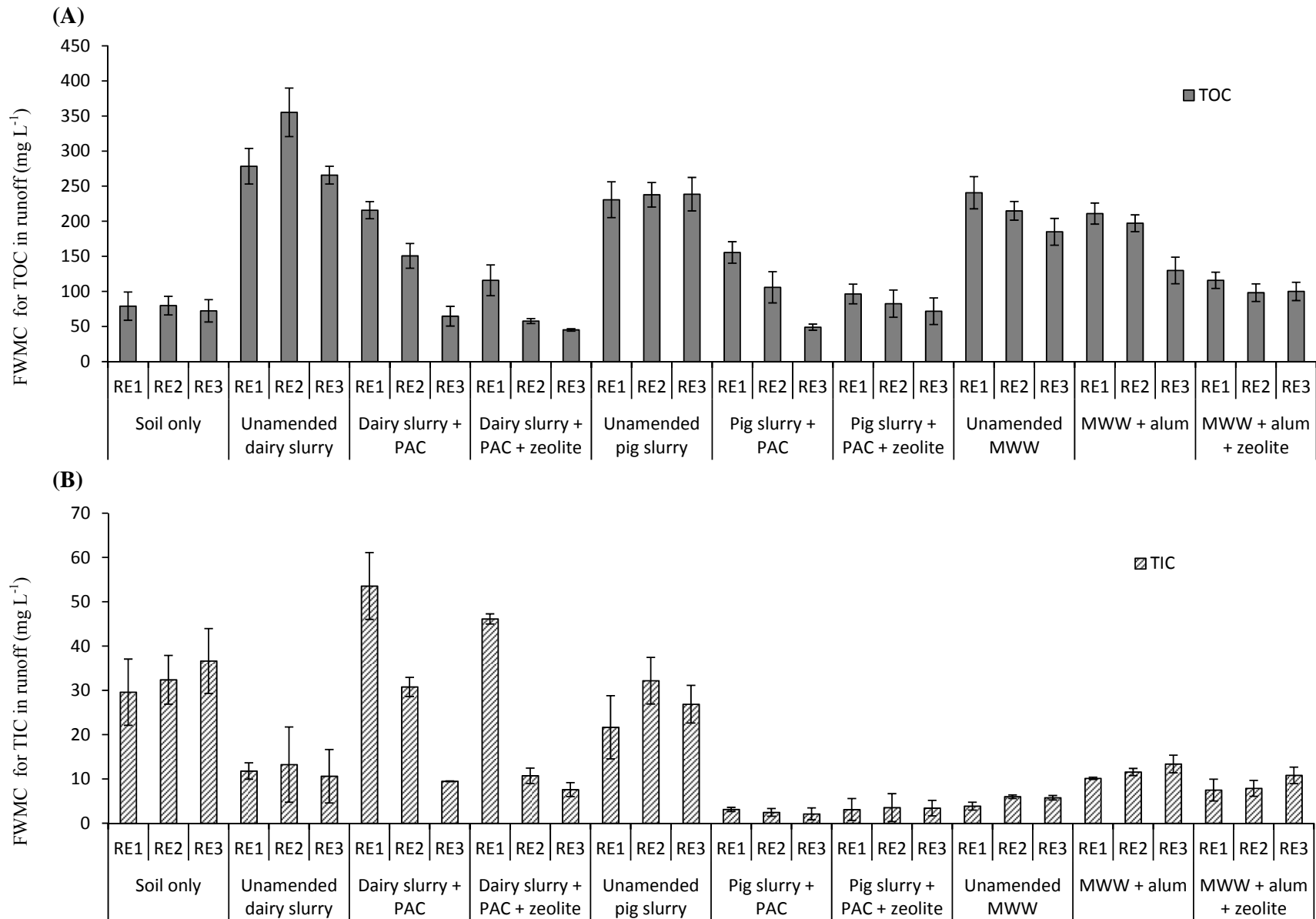
†Values in each column followed by the same letters are not statistically different (p< 0.05) as determined by analysis of variance for all data and all treatments.

**Table 4** Mass balance of total organic carbon (TOC) in runoff boxes during simulated rainfall for (a) unamended slurries, (b) slurries amended with either polyaluminum chloride (PAC) or alum, and (c) slurries amended with zeolite and either polyaluminum chloride (PAC) or alum (dual amended slurries). The flow weighted mean concentrations in runoff (n=3) are averaged over three rainfall events and the amendment application rates are as described in Table 3.

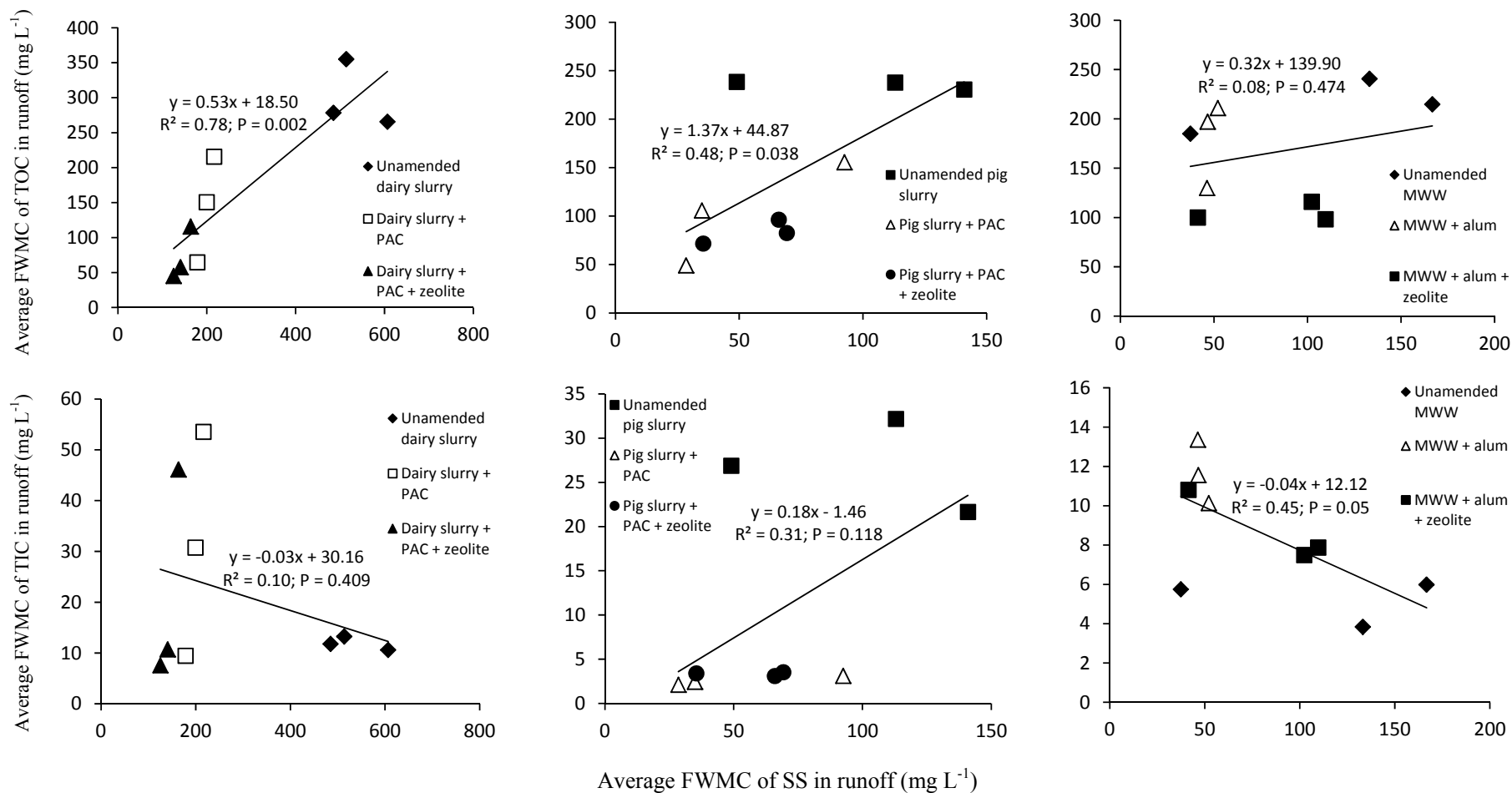
Slurry type	Vol. slurry applied (mL)	Slurry TOC conc. (mg L <sup>-1</sup> )	Mass TOC applied (mg)	Vol. runoff (mL)	Flow weighted mean concentration of TOC in surface runoff from....			Mass TOC in surface runoff from....			Mass TOC in surface runoff as a proportion of mass TOC applied for....		
					(a) unamended slurries	(b) PAC/alum amended slurries	(c) dual amended slurries	(a) unamended slurries	(b) PAC/alum amended slurries	(c) dual amended slurries	(a) unamended slurries	(b) PAC/alum amended slurries	(c) dual amended slurries
					----- (mg L <sup>-1</sup> ) -----			----- (mg) -----			----- % -----		
Dairy slurry	759	15,723	11,939	878	300	144	73	263	126	64	2.2	1.1	0.5
Pig slurry	691	10,471	7,232	956	236	104	84	226	99	80	3.1	1.4	1.1
Milk house wash water	1,125	1,137	1,279	1,041	214	179	105	223	186	109	17.4	14.6	8.5



**Figure 1:** Total organic carbon (TOC) and total inorganic carbon (TIC) removals in batch study tests (n=3) following application of polyaluminum chloride (PAC) to dairy and pig slurries and alum to milk house wash water (MWW). Optimum volumetric ratios for TOC and TIC removals were 0.0256 and 0.0197 PAC:slurry for dairy and pig slurries respectively, and 0.0056 alum:slurry for MWW. Applied volumetric ratios for TOC and TIC removals were 0.0111 and 0.0097 PAC:slurry for dairy and pig slurries, respectively, and 0.0024 alum:slurry for MWW.



**Figure 2:** Histogram of flow weighted mean concentrations (FWMC) (n=3) for **(A)** total organic carbon (TOC) and **(B)** total inorganic carbon (TIC) 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. Error bars indicate standard deviation.



**Figure 3:** Correlation between suspended solid (SS) concentrations and corresponding total organic carbon (TOC) and total inorganic carbon (TIC) concentrations (n=3) for dairy slurry, pig slurry and milk house wash water (MWW) 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 correlation analysis with correlation coefficients (R<sup>2</sup>) and significance (p) indicated.