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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
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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% Al₂O₃) for
44 dairy and pig slurries or liquid aluminum sulfate (alum) (8% Al₂O₃) for MWW. Four
45 treatments under repeated 30 min simulated rainfall events (9.6 mm h⁻¹) 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⁻¹, respectively); alum-amended MWW (3.2 kg t⁻¹), and
49 (4) combined zeolite and PAC-amended dairy (160 and 13.3 kg t⁻¹ zeolite and PAC,
50 respectively) and pig slurries (158 and 11.7 kg t⁻¹ zeolite and PAC, respectively); and

51 combined zeolite and alum-amended MWW (72 and 3.2 kg t⁻¹ zeolite and alum,
52 respectively). The unamended and amended slurries were applied at net rates of 31, 34
53 and 50 t ha⁻¹ 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 μm) and macro (>2000 μm) 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 (CO₂), as well as nitrous oxide (N₂O) 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 = 10¹⁵ 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 CO₂, 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% Al_2O_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 ± 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 ($1.02 \pm 0.07 \text{ g cm}^{-3}$) 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 ($10.4 \pm 0.7 \text{ }^\circ\text{C}$) 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_2 (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 $105 \text{ }^\circ\text{C}$ 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% Al_2O_3) added to the
182 dairy and pig slurries at rates equivalent to 13.3 and 11.7 kg t^{-1} (10.10 and 8.08 mg per
183 runoff box), and commercial grade liquid aluminum sulfate (alum) (8% Al_2O_3) added
184 to the MWW at a rate equivalent to 3.2 kg t^{-1} (3.61 mg per runoff box). Turkish zeolite
185 (clinoptilolite), comprising 66.7% SiO_2 and 10.4% Al_2O_3 , was sieved to 2.36 – 3.35
186 mm and added at rates equivalent to 160, 158, and 72 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 μL were added to approximately 75 mL of dairy and
192 pig slurries, and varying amounts of alum ranging from 50 to 1000 μL 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⁻¹), at an intensity of 9.6
206 ±0.16 mm h⁻¹ (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⁻¹
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⁻¹ for dairy and pig slurries and a volumetric limit of 50 m³ ha⁻¹ 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 μm)
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 ± 0.3 % DM) when compared to the dairy (8.0 ± 0.1 %
241 DM) and pig (2.6 ± 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⁻¹), 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 μm 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 m³ 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

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360

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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.

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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.

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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.

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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 ⁻¹) -----			%
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 ⁻¹)		Correlation coefficient		Chemical added	(2) Maximum removal (mg kg ⁻¹)	
	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.

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

D(U) Unamended dairy slurry

D(P) Dairy slurry amended with polyaluminum chloride (PAC) at 13.3 kg t⁻¹

D(Z+P) Dairy slurry amended with zeolite at 160 kg t⁻¹ and polyaluminum chloride (PAC) at 13.3 kg t⁻¹

P(U) Unamended pig slurry

P(P) Pig slurry amended with polyaluminum chloride (PAC) at 11.7 kg t⁻¹

P(Z+P) Pig slurry amended with zeolite at 158 kg t⁻¹ and polyaluminum chloride (PAC) at 11.7 kg t⁻¹

MWW(U) Unamended milk house wash water

MWW(A) Milk house wash water amended with alum at 3.2 kg t⁻¹

MWW(Z+A) Milk house wash water amended with zeolite at 72 kg t⁻¹ and alum at 3.2 kg t⁻¹

†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 ⁻¹)	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 ⁻¹) -----			----- (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

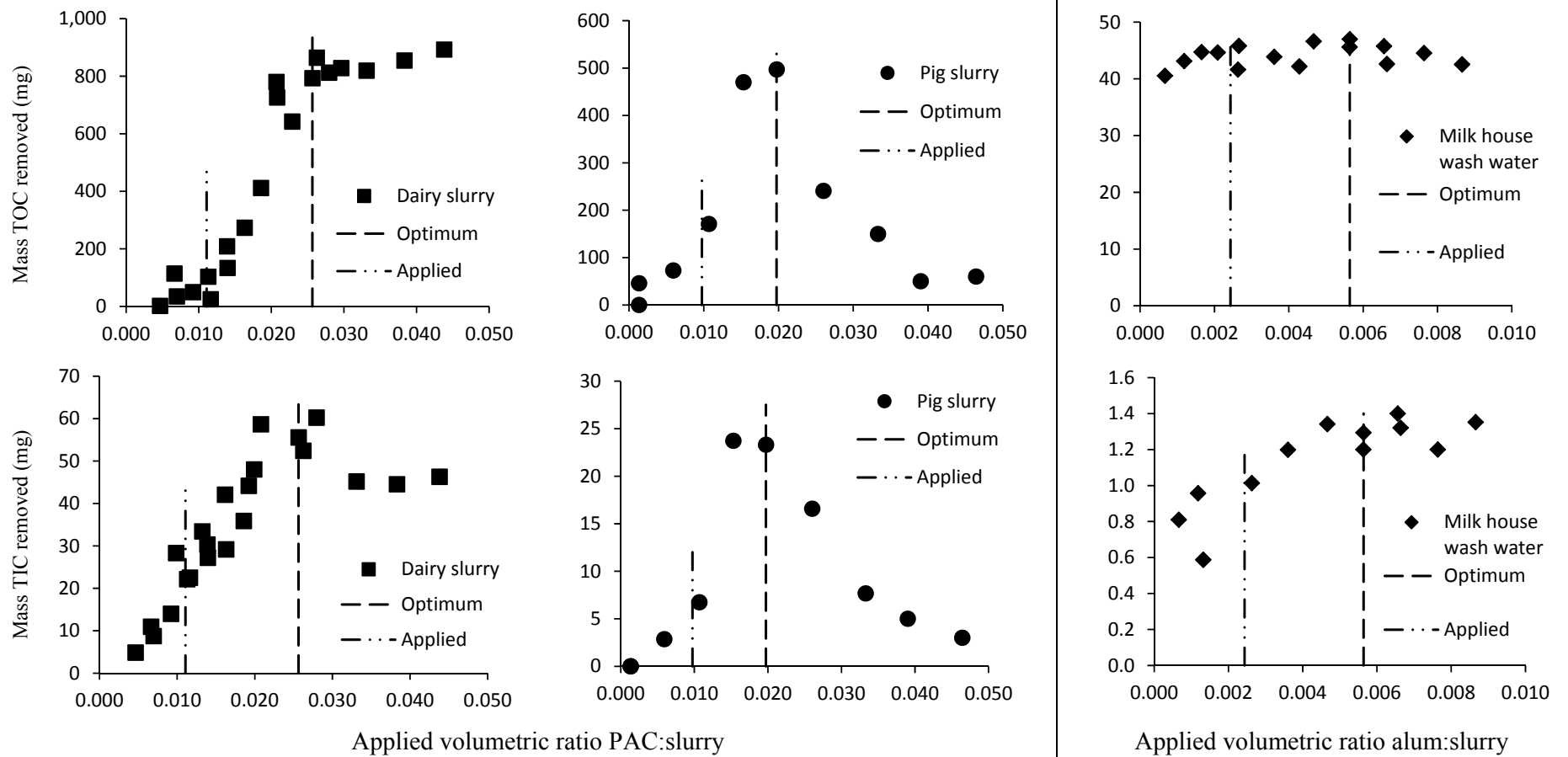


Figure 1: Total organic carbon (TOC) and total inorganic carbon (TIC) removals in batch study tests (n=3) following application of polyaluminum chloride (PAC) to dairy and pig slurries and alum to milk house wash water (MWW). Optimum volumetric ratios for TOC and TIC removals were 0.0256 and 0.0197 PAC:slurry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

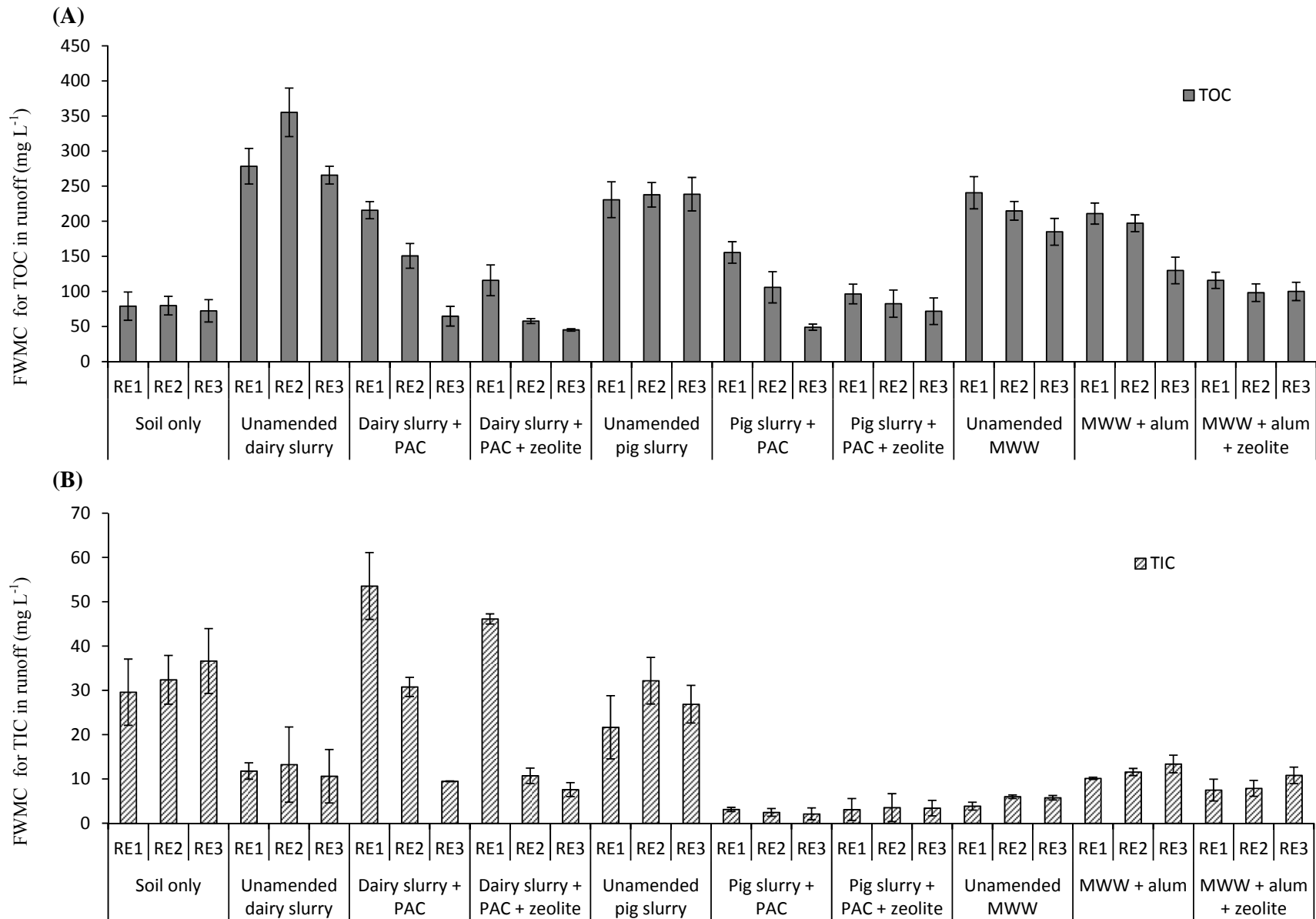


Figure 2: Histogram of flow weighted mean concentrations (FWMC) (n=3) for **(A)** total organic carbon (TOC) and **(B)** total inorganic carbon (TIC) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h. Error bars indicate standard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

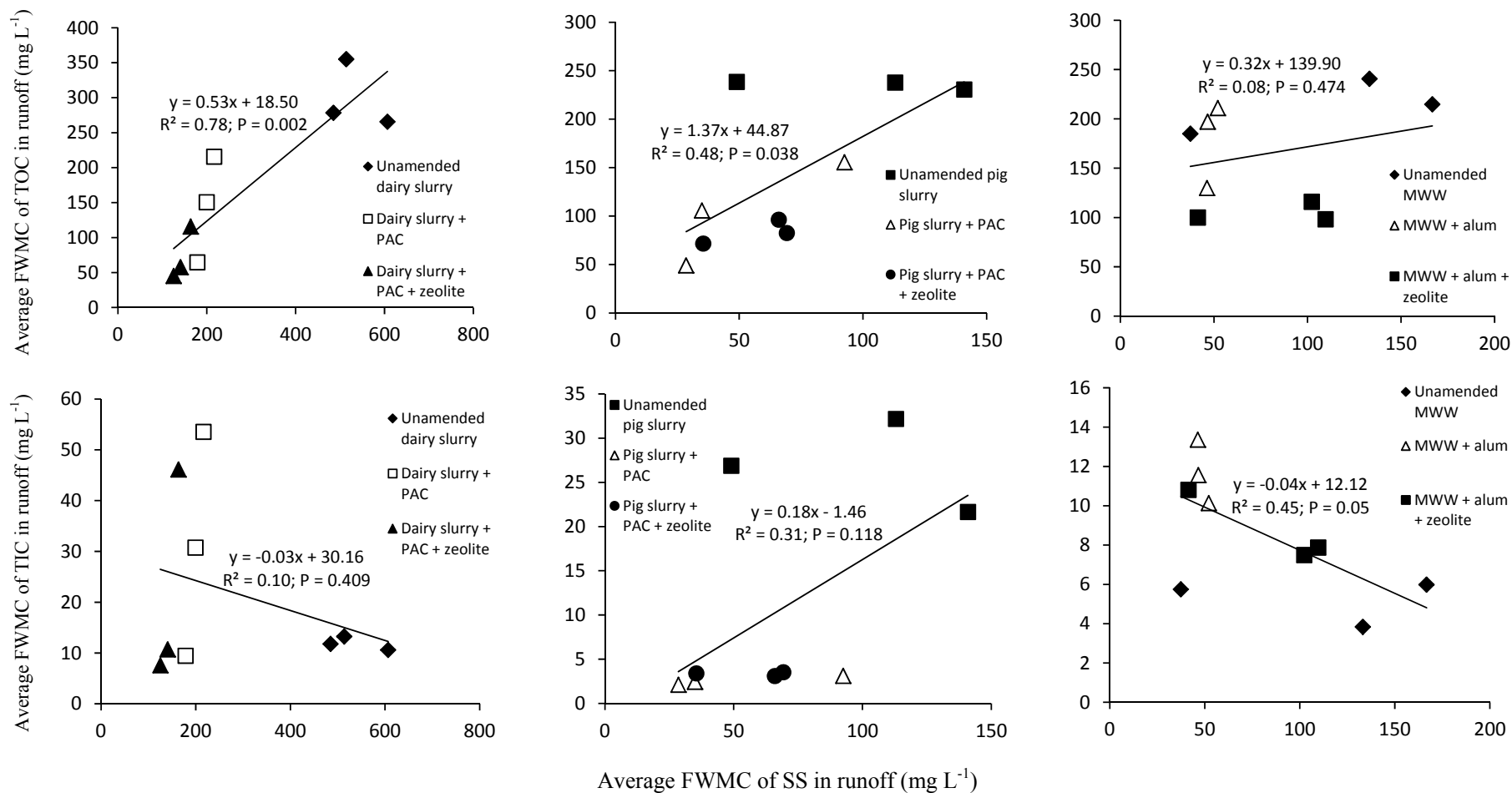


Figure 3: Correlation between suspended solid (SS) concentrations and corresponding total organic carbon (TOC) and total inorganic carbon (TIC) concentrations (n=3) for dairy slurry, pig slurry and milk house wash water (MWW) averaged over all three rainfall events. The data includes unamended wastes, 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^2) and significance (p) indicated.