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Zeolite Combined with Alum and Polyaluminum Chloride Mixed with Agricultural Slurries Reduces Carbon Losses in Runoff from Grassed Soil Boxes

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

Abstract

Carbon (C) losses from agricultural soils to surface waters can migrate through water treatment plants and result in the formation of disinfection by-products, which are potentially harmful to human health. This study aimed to quantify total organic carbon (TOC) and total inorganic C losses in runoff after application of dairy slurry, pig slurry, or milk house wash water (MWW) to land and to mitigate these losses through coamendment of the slurries with zeolite (2.36–3.35 mm clinoptilolite) and liquid polyaluminum chloride (PAC) (10% Al_2O_3) for dairy and pig slurries or liquid aluminum sulfate (alum) (8% Al_2O_3) for MWW. Four treatments under repeated 30-min simulated rainfall events (9.6 mm h^{-1}) were examined in a laboratory study using grassed soil runoff boxes (0.225 m wide, 1 m long; 10% slope): control soil, unamended slurries, PAC-amended dairy and pig slurries (13.3 and 11.7 kg t^{-1}, respectively), alum-amended MWW (3.2 kg t^{-1}), combined zeolite and PAC-amended dairy (160 and 13.3 kg t^{-1} zeolite and PAC, respectively) and pig slurries (158 and 11.7 kg t^{-1} zeolite and PAC, respectively), and combined zeolite and alum-amended MWW (72 and 3.2 kg t^{-1} zeolite and alum, respectively). The unamended and amended slurries were applied at net rates of 31, 34, and 50 t ha^{-1} for pig and dairy slurries and MWW, respectively. Significant reductions of TOC in runoff compared with unamended slurries were measured for PAC-amended dairy and pig slurries (52 and 56%, respectively) but not for alum-amended MWW. Dual zeolite and alum-amended MWW significantly reduced TOC in runoff compared with alum amendment only. We conclude that use of PAC-amended dairy and pig slurries and dual zeolite and alum-amended MWW, although effective, may not be economically viable to reduce TOC losses from organic slurries given the relatively low amounts of TOC measured in runoff from unamended slurries compared with the amounts applied.

Core Ideas

- Slurry application to land may increase carbon concentration in surface runoff.
- PAC, alum, and zeolite were used to mitigate carbon losses in surface runoff.
- Dual application of zeolite and chemical amendments reduced TOC losses.
- Use of amendments may not be economically viable to reduce TOC losses.

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

Application of organic slurries to agricultural soils may result in increased carbon (C) and nutrient losses to ground and surface waters, increased greenhouse gas emissions, and ammonia volatization (Chadwick et al., 2011; Jardé et al., 2007; Li et al., 2013; Morel et al., 2009; O'Flynn et al., 2013). Over the last two decades, elevated levels of dissolved organic C in surface waters have been observed in the United Kingdom (Evans et al., 2005; Freeman et al., 2001; Worrall and Burt, 2007), Europe (Hejzlar et al., 2003; Skjelkvåle et al., 2001), and North America (Burns et al., 2006; Couture et al., 2012; Zhang et al., 2010). These elevated levels are attributed to a variety of influences, including increased air temperatures (Bellamy et al., 2005; Powlson, 2005; Toosi et al., 2014); precipitation (Clark et al., 2007; Dalzell et al., 2005; Hernes et al., 2008; Hongve et al., 2004; Raymond and Oh, 2007); atmospheric influences (Monteith et al., 2007); and changes in agricultural practices, including increased spreading of agricultural slurries to soils (Chen and Driscoll, 2009; Delpla et al., 2011; Oh et al., 2013; Ostle et al., 2009; Owens et al., 2002; Sickman et al., 2010).

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

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

Abbreviations: DM, dry matter; ER, enrichment ratio; FWMC, flow-weighted mean concentration; MWW, milk house wash water; PAC, polyaluminum chloride; SOC, soil organic carbon; SS, suspended solids; TIC, total inorganic carbon; TOC, total organic carbon.

Naidu, 1998) and may result in C losses to ground and surface waters.

Application of organic manures increases soil SOC to a greater extent than inorganic fertilizers (Gattinger et al., 2012; Huang et al., 2010; Li and Han, 2016), and grassed soils offer a greater potential for C storage than tilled or disturbed soils because of their greater protection of micro- (<250 μm) and macroaggregate (>2000 μm)–associated C (Balesdent et al., 2000; Denef et al., 2001, 2007; Zotarelli et al., 2007). Therefore, undisturbed soils such as grasslands offer greater potential to mitigate atmospheric CO_2 as well as N_2O emissions, and it may be environmentally beneficial to focus the application of organic slurries to grassed soils. This, however, would increase the risk of surface runoff and leaching during or immediately after application, and options to mitigate these risks need to be explored.

Total inorganic C (TIC) makes up approximately one third of global soil C stocks (748 Pg, where 1 Pg = 10^{15} g or 1 Gt) in the upper 1 m of soil, with the remainder made up of total organic C (TOC) (1548 Pg) (Batjes, 2014). Although not as agronomically important as TOC, TIC has the potential for enhanced long-term sequestration of atmospheric CO_2, particularly because pedogenic (i.e., formed within soil) carbonates are stable for extremely long periods of time (Manning, 2008; Rawlins et al., 2011). It is becoming increasingly important, therefore, to monitor inorganic as well as organic C in soils to gain a more thorough understanding of soil C dynamics and its impact on the global C cycle.

High concentrations of TOC in surface waters have negative implications for water quality (Seekell et al., 2015; Thrane et al., 2014) and potentially for human health, particularly when these waters are abstracted for potable treatment. High TOC concentrations can act as a transport mechanism for micropollutants such as pesticides and metals (Loux, 1998; Ravichandran, 2004; Rencz et al., 2003) and can be difficult to remove by conventional water treatment (Stackelberg et al., 2004). They can also increase the potential for formation of disinfection by-products after chlorination (Gopal et al., 2007; Hrudey, 2009). Trihalomethanes are the primary disinfection by-products of concern and are considered harmful to human health at concentrations >100 μg L^{-1} (Minear and Amy, 1995; USEPA, 2006). Therefore, removal of TOC at the source is seen as the most effective way of reducing the risk of trihalomethane formation (Crittenden et al., 2012; Minear and Amy, 1995). To date, few studies have quantified C losses to runoff after land application of various agricultural slurries (e.g., Delpla et al., 2011; McTiernan et al., 2001), and no study has assessed the effectiveness of applying amendments to land-applied agricultural slurries to mitigate C losses in runoff to surface waters.

Therefore, the aims of this study were to quantify (i) total C (including TOC and TIC) losses in runoff to surface waters after land application of three types of agricultural slurries (dairy slurry, pig slurry, and milk house wash water [MWW]) and (ii) the effectiveness of applying amendments to the slurries to mitigate these losses. The authors have previously investigated the effectiveness of chemical amendments [polyaluminum chloride (PAC), comprising 10% Al_2O_3 applied to dairy and pig slurries, and alum, comprising $Al_2(SO_4)_3{\cdot}18H_2O$ applied to MWW] applied alone or in combination with zeolite to reduce nitrogen (N), phosphorus (P), and suspended solids (SS) losses from grassed soil in rainfall simulation studies (Murnane et al., 2015). The objective of the current study was to investigate if these amendments, applied at the same rates, were also effective in reducing C losses.

Materials and Methods

Soil

Intact grassed soil samples (n = 45), 0.5 m long, 0.3 m wide, and 0.1 m deep, were cut using a spade and transported on flat timber pallets from a dry stock farm in Galway, Republic of Ireland. The farm had not received manure or fertilizer application for >10 yr before the experiment. The established grass (perennial ryegrass [*Lolium perenne* L.]) was approximately 350 to 400 mm in height and was cut to approximately 25 mm in the laboratory runoff boxes, where it remained alive for the duration of the experiment. The soil pH (6.4 ± 0.3) was measured (n = 3 samples) using a pH probe and a 2:1 ratio of deionized water to soil (Thomas et al., 1996). Particle size distribution was determined using a sieving and pipette method, bulk density (1.02 ± 0.07 g cm^{-3}) was determined using the core method (British Standard [BS] 1377–2) (BSI, 1990a), and organic content (5 ± 2%) was determined by the loss of ignition test (BS 1377–3) (BSI, 1990b). The soil had a sandy loam texture (57 ± 5% sand, 29 ± 4% silt, and 14 ± 2% clay) and was classified as an acid brown earth Cambisol (WRB classification).

Agricultural Slurries

Three types of agricultural slurries were collected in 25-L containers from the Teagasc Agricultural Research Centre, Moorepark, Fermoy, County Cork: (i) dairy slurry taken from a dairy cow slatted unit, (ii) pig slurry taken from the slurry tank of an integrated pig unit, and (iii) MWW taken from a milking parlor washwater collection sump. All slurries were homogenized immediately before collection and were transferred directly to a temperature-controlled room (10.4 ± 0.7°C) in the laboratory. All slurry samples were tested within 24 h of collection (n = 3) for TOC and TIC (Table 1) using the method of oxidation by combustion followed by infrared measurement of CO_2 (BS EN 1484) (BSI, 1997) using a BioTector analyzer (BioTector Analytical Systems Ltd). Total P was measured using persulfate digestion, and dry matter (DM) was measured by drying at 105°C for 24 h (APHA, 2005).

Slurry Amendments

The results of a laboratory study by Murnane et al. (2015) determined the optimum combined chemical and zeolite

Table 1. Slurry characterization for total organic carbon (TOC), total inorganic carbon (TIC), total phosphorus (TP), and dry matter (DM) (n = 3).

Slurry type	TOC	TIC	TP	DM
	mg L^{-1}			%
Dairy slurry	15,723 ± 409†	1,224 ± 33	563 ± 55	8.0 ± 0.1
Pig slurry	10,471 ± 640	392 ± 47	619 ± 30	2.6 ± 0.1
Milk house wash water	1,137 ± 75	54 ± 5	52 ± 11	0.7 ± 0.3

† Values are mean ± SD.

application rates for reductions in ammonium N (NH_4–N) and orthophosphate (PO_4–P), and these were used in the current study. The amendments applied were commercial-grade liquid PAC (10% Al_2O_3) added to the dairy and pig slurries at rates equivalent to 13.3 and 11.7 kg t^{-1} (10.10 and 8.08 mg per runoff box) and commercial-grade liquid aluminum sulfate (alum) (8% Al_2O_3) added to the MWW at a rate equivalent to 3.2 kg t^{-1} (3.61 mg per runoff box). Turkish zeolite (clinoptilolite), comprising 66.7% SiO_2 and 10.4% Al_2O_3, was sieved to 2.36 to 3.35 mm and added at rates equivalent to 160, 158, and 72 kg t^{-1} (121.5, 109.4 and 81 g per runoff box) to the dairy and pig slurries and MWW, respectively.

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

Rainfall Simulation Study

Aluminum runoff boxes (1 m long, 0.225 m wide, and 0.05 m deep, with side walls 0.025 m higher than the soil surface) were placed at a 10% slope (representative of local terrain) to the horizontal under the rainfall simulator ($n = 3$). Each runoff box had 5-mm-diameter drainage holes located at 0.3-m intervals along the base, which was covered with muslin cloth to prevent soil loss. Rainfall was generated using a mains water supply (pH 7.7 ± 0.2; electrical conductivity, 0.435 dS m^{-1}) at an intensity of 9.6 ± 0.16 mm h^{-1} (representative of a 2-yr, 1-h rainfall event) and average uniformity coefficient of 0.84 over the experimental area (2.1 m × 2.1 m) using a single 1/4HH-SS14SQW nozzle (Spraying Systems Co.) placed approximately 3.4 m above the soil surface. The intact grassed soil samples were trimmed by hand (0.45–0.5 m long, 0.225 m wide, and 0.05 m deep), placed firmly in the runoff boxes, saturated from the base, and then left to drain for 24 h to replicate field capacity conditions. At this point (t = 24 h), amended and unamended slurries were stirred and applied by even and consistent hand spreading in repeated figure eight patterns to the grassed soil at rates, net of applied amendments, equivalent to 31, 34, and 50 t ha^{-1} (759, 691, and 1125 g per runoff box) for pig and dairy slurries and MWW and left for 48 h. The applied rates were the maximum permissible based on a limit of 19 kg P ha^{-1} for dairy and pig slurries and a volumetric limit of 50 m^3 ha^{-1} for MWW (SI No. 31) (BSI, 2014). In addition, unamended soil boxes ($n = 3$) were used as controls. At t = 72, 96, and 120 h, successive rainfall events were applied (RE1, RE2, and RE3, respectively), each lasting 30 min after continuous runoff was observed. During each rainfall simulation, the surface runoff was collected at time intervals of 10, 20, and 30 min, and TOC and TIC were measured immediately using a BioTector analyzer. Subsamples taken at 5-min intervals were thoroughly mixed and measured for SS by vacuum filtration through Whatman GF/C glass fiber filters (pore size, 1.2 μm) (APHA, 2005).

Data Analysis

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

Results and Discussion

Batch Studies and Amendment Application Rates

The applied PAC/alum rates, based on N and P removals (Murnane et al., 2015), were less than those that provided optimum TOC and TIC removals for all slurries except for MWW, where increased application of alum did not improve TOC removal rates (Fig. 1). This was most likely due to the reduced opportunity for alum to coagulate the SS in the more dilute MWW (0.7 ± 0.3% DM) when compared with the dairy (8.0 ± 0.1% DM) and pig (2.6 ± 0.1% DM) slurries. The batch studies also showed that a 2.3-fold increase in the PAC application (from applied volumetric ratio of 0.0111 to 0.0256) resulted in a corresponding eightfold increase in TOC removal from dairy slurry (100–800 mg). Similarly, for pig slurry, an approximate doubling of the PAC application rate (from volumetric ratio of 0.0097 to 0.0197) resulted in a corresponding approximately threefold increase in TOC removal (170–500 mg) (Fig. 1). The maximum zeolite adsorption capacities for TOC and TIC (Table 2) indicate that the ability of zeolite to remove TOC might be affected by the DM of the slurries (Table 1), with the highest removals from MWW (the most dilute slurry) followed by pig and dairy slurries. Therefore, the batch studies indicated that the effectiveness of PAC/alum applications to remove TOC increased with increasing slurry DM content, and, conversely, the effectiveness of zeolite to remove TOC decreased with increasing slurry DM content.

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

Rainfall Simulation Study

Significant ($p < 0.001$) increases in FWMCs of TOC were observed for all unamended slurry applications over the

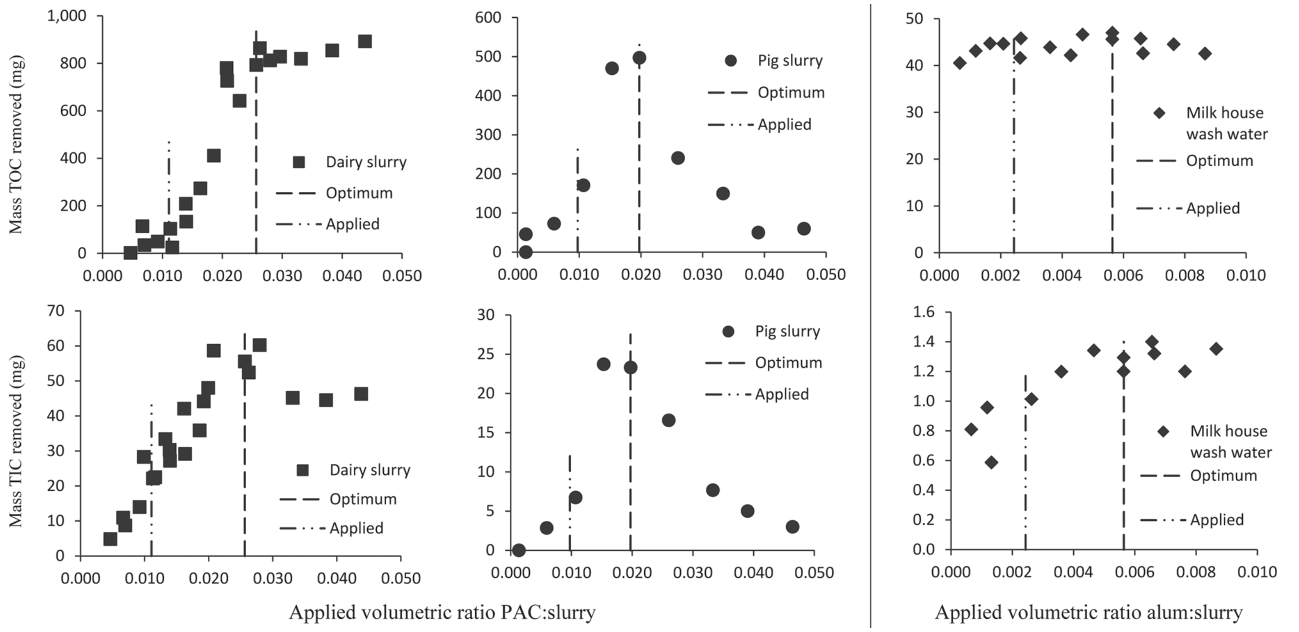

Fig. 1. Total organic C (TOC) and total inorganic C (TIC) removal in batch study tests (*n* = 3) after application of polyaluminim chloride (PAC) to dairy and pig slurries and alum to milk house wash water (MWW). Optimum volumetric ratios for TOC and TIC removals were 0.0256 and 0.0197 PAC/slurry for 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.

three rainfall events when compared with the control soil and were highest for dairy slurry followed by pig slurry and MWW (Fig. 2). The higher TOC content of the dairy slurry compared with the pig slurry and its higher application rate (34 vs. 31 t ha^{-1}) contributed to the higher FWMC in runoff. Total organic C concentrations were reduced compared with the unamended slurries ($p < 0.001$) after application of PAC-amended dairy and pig slurries, but the reductions for alum-amended MWW were not significant (Fig. 2; Table 3). Significant ($p < 0.05$) reductions in TOC were measured for MWW amended with zeolite and alum when compared with alum amendments only and for dairy slurry amended with zeolite and PAC when compared with PAC amendments only. However, pig slurry amended with zeolite and PAC was not significantly lower than that amended with PAC only. Average reductions in FWMCs of TIC in runoff compared with unamended slurries over the three rainfall events were significant only for pig slurry ($p < 0.001$) (increases in TIC were observed for dairy slurry and MWW); however, average TIC concentrations remained below those of the control soil for all slurries and all treatments (Table 3).

Relationship between Suspended Solids and C Losses in Runoff

The average FWMC of TOC in runoff was positively correlated with corresponding SS concentrations (Murnane et al. [2015] and Fig. 3) for both unamended and amended dairy and pig slurries ($R^2 = 0.78$ and 0.48, respectively) but was not correlated with MWW (Fig. 3). In contrast, there was a negative correlation between SS concentrations and average FWMC of TIC in runoff for dairy slurry, a weak positive correlation for pig slurry ($R^2 = 0.31$), and a negative correlation for MWW (Fig. 3). Chemical amendments flocculate slurry particles, which, once entrained on the soil surface, have a high resistance to being washed off during repeated rainfall events (Kang et al., 2014; McCalla, 1944). Particulate organic matter in land-applied slurries contain colloidal particles, which have a large specific surface area and provide the greatest number of sites for sorption of pollutants, including C. In a particle size fractionation study of pig slurry, Aust et al. (2009) found that particle size fractions <63 μm contained 50% of slurry DM, and it is colloidal particles of this size that are usually released in surface runoff after land application of agricultural manures immediately after the start of a rainfall event or in high-intensity storms (Delpla et al., 2011). Studies to measure the enrichment ratios (ERs) (ratio of C

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 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 were modeled 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		Correlation coefficient		Chemical added	(2) Maximum removal	
	TOC	TIC	TOC	TIC		TOC	TIC
	mg kg^{-1}					mg kg^{-1}	
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

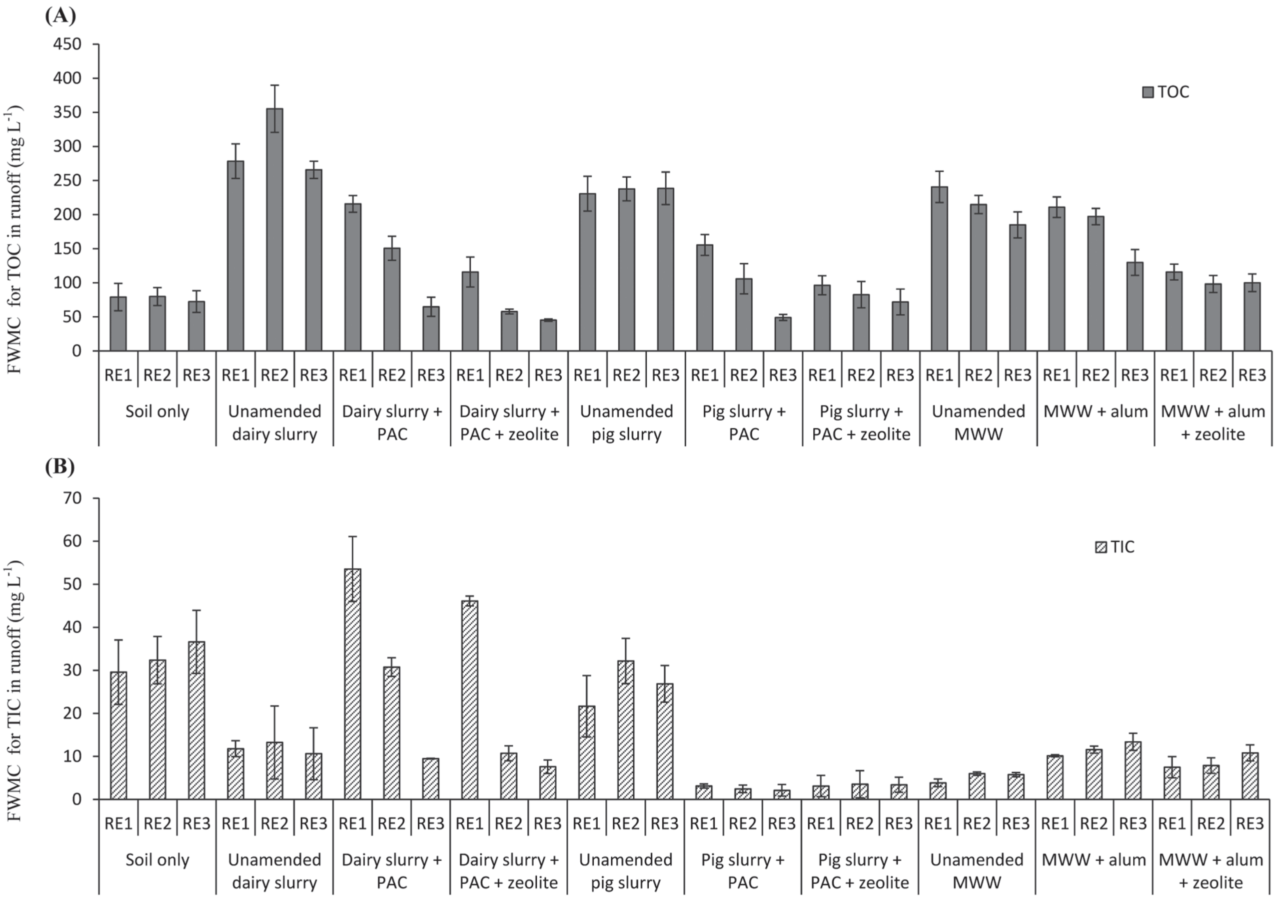

Fig. 2. Histogram of flow-weighted mean concentrations (FWMCs) (*n* = 3) for (A) total organic C (TOC) and (B) total inorganic C (TIC) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h, and rainfall event 3 (RE3) at t = 120 h. Error bars indicate SD.

concentration in eroded sediment to the original concentration of sediment from where the eroded sediment originated) of C in runoff (Jacinthe et al., 2004; Jin et al., 2008) have reported ERs ranging from 1.01 to 3.4, whereas ERs between 1.16 and 2.33 in particles mobilized by rainfall splash under natural precipitation have also been measured (Beguería et al., 2015). Polyaluminum chloride was most effective at removing TOC (even though the applied rate was less than the optimum; see Fig. 1) and SS from dairy slurry, which had the highest DM content (8%). In contrast, alum was least effective at removing TOC from MWW, which had the lowest DM (0.7%). This indicated that PAC had a greater opportunity to coagulate the C-enriched colloidal particles in the dairy slurry but was less able to coagulate the pig slurry (2.6% DM) because less of it remained on top of the

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).

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

† D(P), dairy slurry amended with polya+luminum chloride (PAC) at 13.3 kg t^{-1}; D(U), unamended dairy slurry; D(Z+P), dairy slurry amended with zeolite at 160 kg t^{-1} and PAC at 13.3 kg t^{-1}; MWW(A), milk house wash water amended with alum at 3.2 kg t^{-1}; MWW(U), unamended milk house wash water; MWW(Z+A), milk house wash water amended with zeolite at 72 kg t^{-1} and alum at 3.2 kg t^{-1}; P(P), pig slurry amended with PAC at 11.7 kg t^{-1}; P(U), unamended pig slurry; P(Z+P), pig slurry amended with zeolite at 158 kg t^{-1} and PAC at 11.7 kg t^{-1}.

‡ Values in each column followed by the same letters are not statistically different ($p < 0.05$) as determined by ANOVA for all data and all treatments.

§ No values apply.

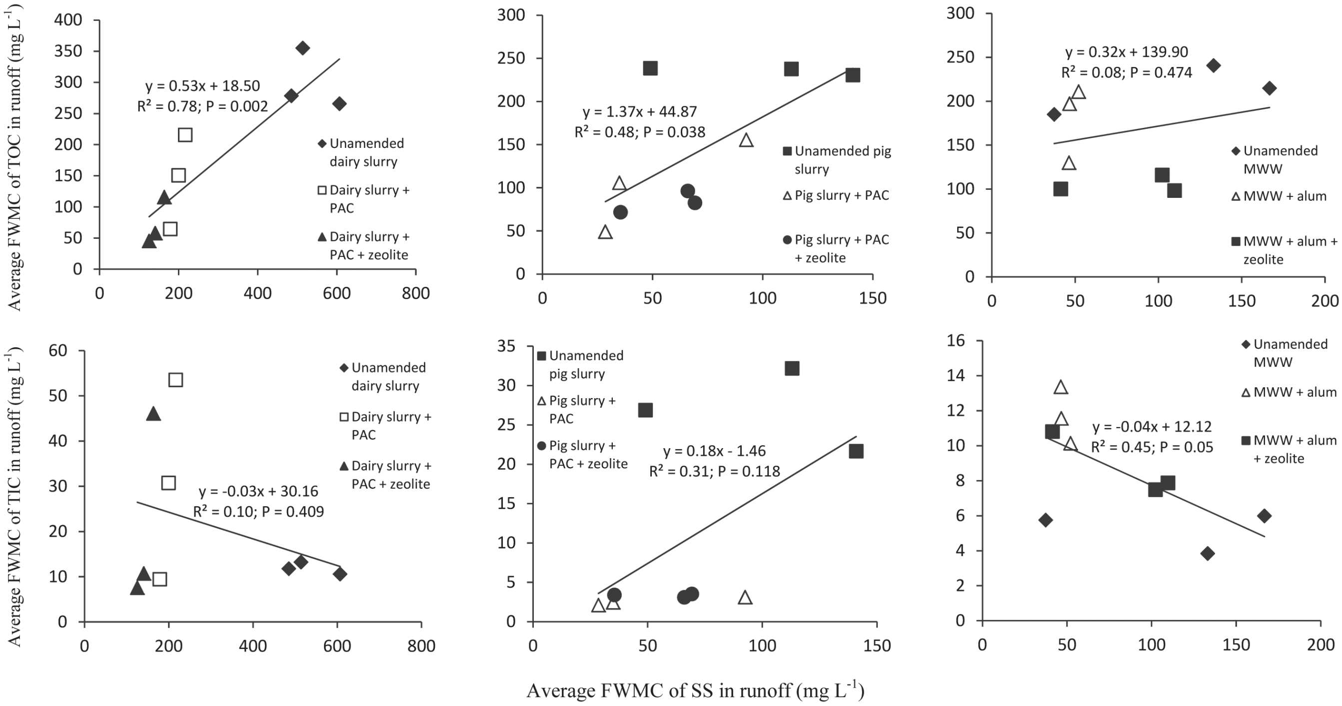

Fig. 3. Correlation between suspended solids (SS) concentrations and corresponding total organic C (TOC) and total inorganic C (TIC) concentrations (n = 3) for dairy slurry, pig slurry, and milk house wash water (MWW) averaged over all three rainfall events. The data include unamended wastes, wastes amended with polyaluminim chloride (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.

soil during the rainfall events. Similarly, alum was least able to coagulate the dilute MWW and was therefore least effective in mitigating TOC losses. Application of combined zeolite and alum amendments significantly ($p < 0.05$) reduced TOC in runoff from MWW when compared with alum amendments only (Table 3; Fig. 2). This indicates that zeolite has a role in C sequestration in runoff, particularly from slurries with a low DM content, and corroborates the results of the zeolite adsorption tests performed in the batch studies (Table 2).

Implications for Use of Amendments at Field-Scale

In this study, the use of dual zeolite and PAC/alum amendments with land-applied organic slurries has been shown to be reasonably effective in retaining a proportion of the TOC lost in runoff (range, 51–76%) (Table 3) under simulated rainfall even though the PAC/alum was not applied at optimum TOC removal rates (Fig. 1). However, in a wider context, the amounts of TOC lost in surface runoff from the unamended slurries as a proportion of the amounts applied were quite low (2.2, 3.1 and 17.4% from dairy and pig slurries and MWW, respectively), and these losses were reduced for all slurries after application of either PAC/alum amendments or dual amendments of zeolite and either PAC/alum, with the highest removal rate of 8.9% (from 17.4 to 8.5%) for MWW (Table 4). The estimated costs per m^3 of applying the amendments (in Ireland) for dairy and pig slurries and MWW, respectively, are €190, €188, and €84 for dual zeolite and either PAC or alum and €6.40, €5.60, and €0.80 for PAC/alum amendments only (Murnane et al., 2015). Although it is recognized that these costs will vary regionally, it is clear that the economic benefits of C sequestration by application of dual zeolite and PAC/alum amendments may be prohibitive for all slurries. The benefits of applying PAC only to the dairy and pig slurries and alum to the MWW for C removal may also be uneconomical at the rates indicated.

Table 4. Mass balance of total organic carbon (TOC) in runoff boxes during simulated rainfall for unamended slurries, slurries amended with either polyaluminum chloride (PAC) or alum, and slurries amended with zeolite and either 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	Slurry TOC conc.	Mass TOC applied	Vol. runoff	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		
					Unamended slurries	PAC/alum amended slurries	Dual-amended slurries	Unamended slurries	PAC/alum amended slurries	Dual-amended slurries	Unamended slurries	PAC/alum amended slurries	Dual-amended slurries
	mL	mg L^{-1}	mg	mL		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

Conclusions

Dual application of zeolite and either PAC to dairy and pig slurries or alum to MWW reduced TOC in runoff from grassed soil runoff boxes under repeated simulated rainfall. Increases in TOC in runoff were measured after application of unamended slurries when compared with the control soil. Significant ($p < 0.001$) reductions of TOC in runoff were observed by the use of PAC amendments for dairy and pig slurries and by use of dual zeolite and alum amendments to MWW. Reductions in TIC were significant only for PAC-amended pig slurry ($p < 0.001$) but remained below those of the control soil for all slurries and all treatments. Total organic C losses were correlated to SS concentrations in runoff and indicated that the C removal mechanisms depend on the DM content of the slurry. Given the relatively low amounts of TOC measured in runoff from unamended slurries compared with the amounts applied, widespread application of amendments may not be economically viable at field-scale to reduce TOC losses.

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