NATIONAL UNIVERSITY OF IRELAND, GALWAY

COMBINED ZEOLITE AND CHEMICAL AMENDMENTS MIXED WITH AGRICULTURAL WASTES TO REDUCE SURFACE AND LEACHING LOSSES OF NUTRIENTS AND GREENHOUSE GAS EMISSIONS, AND BIOFILTER TREATMENT OF DAIRY SOILED WATER

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Abstract

Agricultural activity is a major source of nutrient emissions to surface and ground waters and a significant contributor to greenhouse gas emissions. Despite legislation to improve terrestrial water quality, prescribed targets are not being met. This is against a background of more intensive farming practices such as concentrated animal feeding operations, which have led to large volumes of manures being generated in relatively small areas and spread at rates that exceed plant nutrient demand. The competing demands of providing more food from the same land area, while simultaneously reducing environmental impacts, is a major challenge. While many mitigation measures to reduce nutrient losses, such as crop and land management, have been put forward, these alone will not achieve the necessary improvements in water and air quality. The main nutrients of concern are phosphorus (P), which mainly contributes to coastal and freshwater eutrophication, and nitrogen (N), which has adverse impacts on human and livestock health through leaching to groundwater. Increased losses of carbon (C) also adversely impact the atmosphere through greenhouse gas emissions. New techniques which are sustainable, economical, and which do not negatively impact the atmosphere, aquatic ecosystems or human and animal health, are therefore required to reduce this form of non-point agricultural pollution. Similarly, a greater understanding of the removal mechanisms and factors affecting the performance of existing treatment technologies, such as aerobically operated farm filters, is needed.

This laboratory-based study examined the effectiveness of applying combined zeolite and either polyaluminum chloride (PAC) or alum amendments to reduce losses of N, P, C and suspended solids (SS) from surface applied dairy and pig slurries, and dairy soiled water (DSW), when subjected to varying interval rainfall events. Traditionally, such studies aimed to reduce only P in the surface runoff; however, this study aimed to identify an optimal amendment to the slurries and DSW to simultaneously reduce N, P, C and SS. Once an optimal rate of amendment was determined, their impact – if any – on leaching losses of N, P and C, and on emissions of carbon dioxide (CO_2) and methane (CH_4), were quantified. Separately, a passive filter study using woodchip and sand media to investigate the impacts of media depth, organic loading rates (OLRs), and media type to treat DSW, was also undertaken.

The study concluded that combined use of zeolite and chemical amendments when mixed with dairy and pig slurries and DSW, reduced losses of N, P and SS in surface runoff to a much greater extent than those from unamended slurries. The combined amendments were most effective when mixed with dairy slurry, followed by pig slurry, and were least effective when used with DSW. The impact of the amendments was correlated with the dry matter (DM) content of the slurries and the relative effectiveness of the amendments to flocculate P, N and SS-enriched slurry particles. Although the amendments were also effective in reducing C losses, their use may not be economically viable, given the relatively low amounts of C measured in runoff from unamended slurries compared with the amounts applied. Use of the combined amendments did not reduce leaching losses of N, P and C, or gaseous emissions of CO_2 and CH_4 from pig slurries and DSW, when compared to unamended slurries. While they reduced leaching losses of C from dairy slurries, they also increased CO_2 emissions. The greatest short term threat of nutrient leaching and gaseous emissions of CO_2 and CH_4 was posed by pig slurry, in both amended and unamended forms.

Intermittently loaded woodchip filters were assessed to be more economically and environmentally effective in treating DSW than sand filters; however, their removal mechanism for all contaminants was physical as opposed to biological. While the sand filters nitrified DSW effluent [43±18 mg nitrate-N (NO_3-N) L^{-1}] for the first 85 days of operation, concentrations reduced thereafter to 7.2±1.6 mg NO_3-N L^{-1}. The woodchip filters did not nitrify the effluent, even at relatively low loadings of 35 g chemical oxygen demand (COD) m^{-2} d^{-1}. The final filtered effluent from both sand and woodchip filters, however, was above the concentrations at which it may be legally discharged to receiving waters. Options for its reuse may be to use the treated effluent in irrigation and, in time, to incorporate the spent timber residue into the soil.

The potential of mixing zeolite and chemical amendments with agricultural slurries to mitigate environmental impacts must be considered in the context of traditional conservation and nutrient management practices, which would appear to be the most cost effective strategies over the long term. The N, P, and C mitigation measures described in this study may provide more immediate water quality benefits, at overloaded 'legacy' sites or 'critical source areas', where manure additions are already restricted to crop removal rates. Prior to use of the new techniques described in this study, a cost-benefit analysis of applying amendments to organic wastes, and to on-farm filter treatment of DSW will be essential in the context of whole-farm and watershed-scale nutrient management. Such an analysis should only be carried out after long term field-scale studies, and should also address management and legislative issues related to discharge consents for on-farm treated agricultural wastes and to selected use of manure amendments.

Declaration

This dissertation is the result of my own work, except where explicit reference is made to the work of others, and has not been submitted for another qualification to this or any other university.

John Murnane

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Abbreviations

Al	Aluminium
AAS	Atomic Adsorption Spectrometry
ACP	Agricultural Catchments Programme
AD	Anaerobic Digestion
Al_2O_3	Aluminium Oxide
Anion	Negatively charged ion
ANOVA	Analysis of Variance
AOB	Ammonium Oxidising Bacteria
B	Boron
BA	Bottom Ash
B_aO	Barium Oxide
BOD	Biochemical Oxygen Demand
C	Carbon
Ca	Calcium
$Ca(OH)_2$	Lime
C_aO	Calcium Oxide
CEC	Cation Exchange Capacity
CH_4	Methane
Cl	Chloride
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
CSO	Central Statistics Office
CW	Constructed Wetland
CWA	Clean Water Act
DIC	Dissolved Inorganic Carbon
DM	Dry Matter
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
DRP	Dissolved Reactive Phosphorus
DSW	Dairy Soiled Water

DUP	Dissolved Unreactive Phosphorus
EC	European Commission
EPA	Environmental Protection Agency
ER	Enrichment Ratio
EU	European Union
FA	Fly Ash
FAO	Food and Agriculture Organization (of the United Nations)
Fe	Iron
Fe_2O_3	Iron (III) Oxide
FGD	Flue Gas Desulphurization (by-product)
FWMC	Flow-weighted mean concentration
FWS	Free Water Surface
GHG	Greenhouse Gas
Gt	Gigatonne
HCL	Hydrochloric Acid
HLR	Hydraulic Loading Rate
HRT	Hydraulic Retention Time
ICIS	International Standard Industrial Classification
ICP- OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IPCC	Intergovernmental Panel on Climate Change
K	Potassium
K_2O	Potassium Oxide
LOI	Loss on Ignition
Mg	Magnesium
M_gO	Magnesium Oxide
MLSS	Mixed Liquor Suspended Solids
Mn	Manganese
M_nO	Manganese Oxide
MWW	Milk-house Wash Water
N	Nitrogen
N_2O	Nitrous Oxide
N_a	Sodium

Na_2O	Sodium Oxide
$NH3^+$	Ammonia
$NH4^+$	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
NOB	Nitrite Oxidising Bacteria
N_{org}	Organic Nitrogen
OLR	Organic Loading Rate
OM	Organic Matter
P	Phosphorus
P_2O_5	Phosphorus Pentoxide
PAC	Poly-aluminum chloride
Pg	Petagram (10^{15}g)
Pm	Morgan’s Phosphorus
PN	Particulate Nitrogen
PO_4-P	Orthophosphate
POM	Programmes of Measures
PP	Particulate Phosphorus
PRI	Permeable Reactive Interceptor
RCF	Relative Centrifugal Force
RE	Rainfall Event
S	Sulfur
SBR	Sequencing Batch Reactors
SI	Statutory Instrument
SIC	Soil Inorganic Carbon
S_iO_2	Silicon Dioxide
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
SPSS	Statistical Package for the Social Sciences
S_rO	Strontium Oxide
SS	Suspended Sediment (Solids)
SSF	Sub-Surface Flow
STP	Soil Test Phosphorus

SVI	Sludge Volume Index
TC	Total Carbon
TDP	Total Dissolved Phosphorus
THM	Trihalomethane
TIC	Total Inorganic Carbon
T_iO_2	Titanium Dioxide
TN	Total Nitrogen
TN_d	Total Dissolved Nitrogen
TOC	Total Organic Carbon
TON	Total Oxidized Nitrogen
TP	Total Phosphorus
UNEP	United Nations Environment Program
VSB	Vegetated Submerged Bed
WEP	Water extractable phosphorus
WFD	Water Framework Directive
WRB	World Reference Base (for soils)
WSOC	Water Soluble Organic Carbon

Chapter 1 – Literature Review

1.1 Background

The global agricultural industry, comprising 4.9 billion hectares, greater than 570 million farms, and employing *c.* 2.6 billion people directly and indirectly (Alston and Pardey, 2014; Hurni et al., 2015), has grown significantly over the past three decades, with output increasing from 0.6 to 3.2 trillion US dollars between 1985 and 2015 (World Bank, 2016). This coincides with a growing world population which has more than doubled from approximately 3 billion in 1960 to almost 7.4 billion today (Fig. 1.1). Agricultural growth, particularly since 2000, is driven largely by an increased demand for cereal production, mainly rice, wheat and maize (Grassini et al., 2013), in order to sustain an increased demand for livestock products and biofuels (Soussana, 2014).

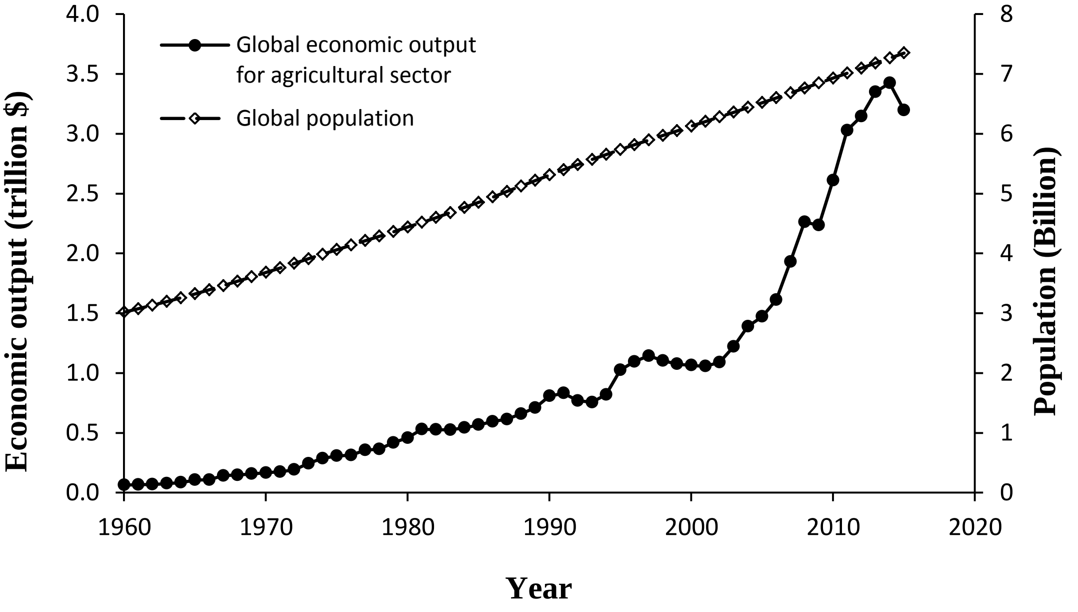

Figure 1.1 Global economic outputs for the agricultural sector and global population between 1960 and 2015. The economic data (U.S. dollars) corresponds to International Standard Industrial Classification (ISIC) divisions 1-5 and includes forestry, hunting, and fishing, as well as cultivation of crops and livestock production. The graphs are generated using economic data from the World Bank *(accessed on 24.11.16 at http://data.worldbank.org/indicator/NV.AGR.TOTL.CD)* and population data from the Food and Agriculture Organization of the United Nations (FAO) *(accessed on 24.11.16 at http://faostat3.fao.org/download/O/OA/E).*

Much of the growth in demand for livestock products is a direct consequence of increased incomes, particularly in developing countries. As incomes increase, people tend to eat fewer grain-based foods and more meat and high value foods. These dietary changes are also largely influenced by increased urbanisation, as since 2007 more than half the world population live in cities (Orsini et al., 2013).

In the European Union (EU), there are 10.8 million farms of average size of 16.1 ha and approximately 34% of the agricultural land is used for permanent grassland or meadow (Eurostat, 2015). In Ireland the agricultural sector exported approximately €9 billion worth of agri-food and drink (about 8.4% of Ireland's exports) in 2015, and is dominated by dairy and beef cattle production from managed grassland covering an area in excess of 4 million ha (Fig. 1.2; CSO, 2016). There are almost 7 million cattle, 1.5 million pigs and 5.1 million sheep in the country, which produce an estimated 18.2, 3.0 and 1.7 million tonnes of manure annually (Hennessy et al., 2011). The pig industry is concentrated in localised areas throughout the country, with 50% of the national sow herd concentrated in Longford, Tipperary, Cork and Cavan. High densities of pig farms results in a surplus of pig manure in these areas, which must be transported to less dense areas for landspreading. This is reflective of the pig industry in the EU with 30% of sows located in a major pig production basin which stretches from Denmark, through north western Germany and the Netherlands to Vlaams Gewest in northern Belgium (Marquer, 2010).

Agriculture, nationally, regionally and globally, contributes significant amounts of nutrients to terrestrial ecosystems at rates that are likely to increase if past practices continue to be used to achieve increased production rates (Tilman et al., 2002). Intensification of agricultural systems increases the environmental impact of food production with larger livestock production units resulting in higher local emissions to air and groundwater (Peterson et al., 2007). Tegtmeier and Duffy (2004) reported that agricultural production in the United States (U.S.) negatively impacts water, soil, air, wildlife and human health at an estimated cost of $5.6 to $16.9 billion per year.

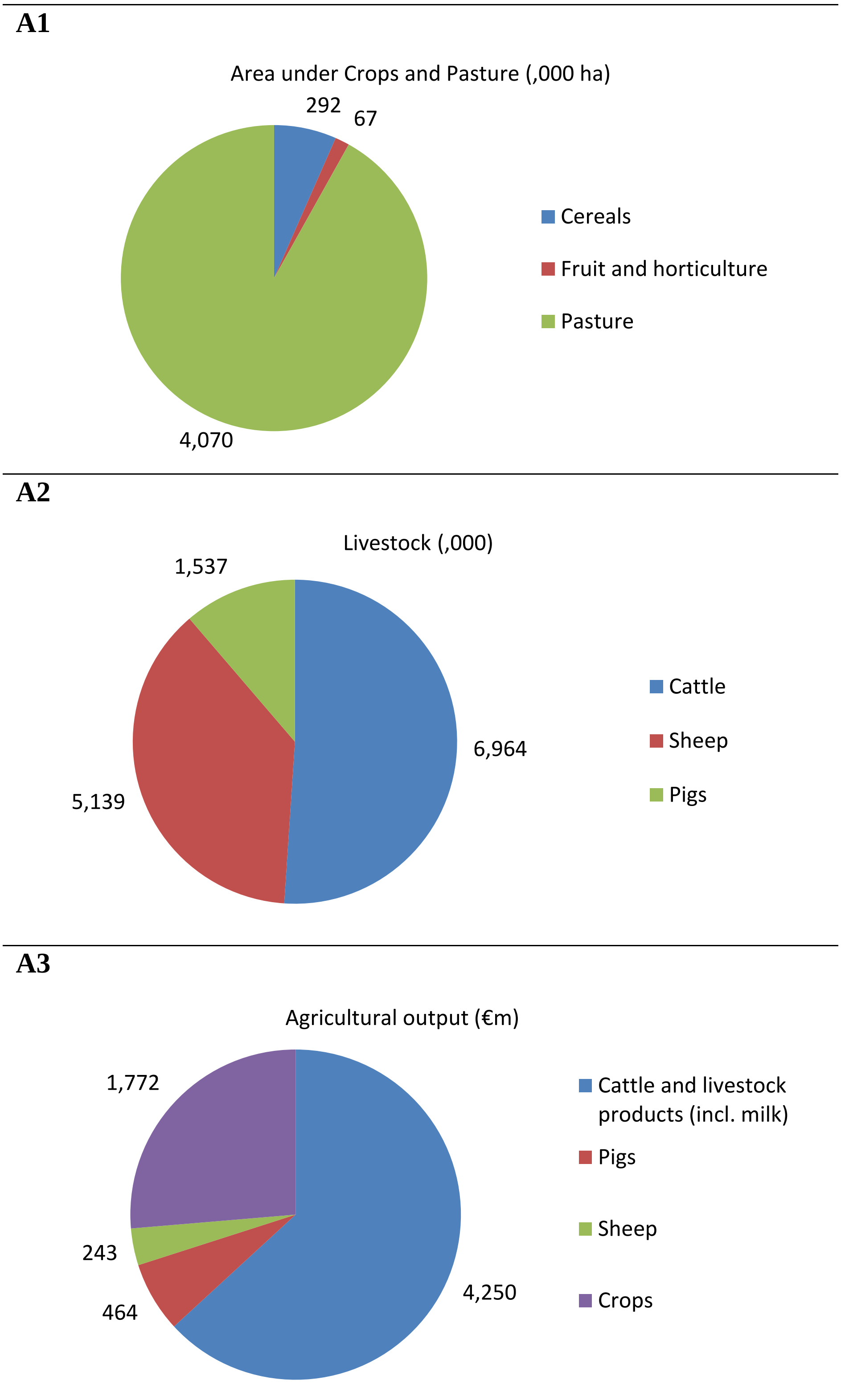

Figure 1.2 Area (‘000 ha) under crops and pasture (A1); number of livestock (‘000) (A2); and economic output (€m) for each sector (A3) in Ireland in 2015.The graphs are generated using economic data from the CSO, 2016 *(http://www.cso.ie/en/releasesandpublications/ep/p-syi/psyi2016/agri/).(accessed February 2017)*

Agriculture is a significant source of land degradation (Nkonya et al., 2011) and anthropogenic global greenhouse gas (GHG) emissions, contributing 25% carbon (C) (largely from deforestation), 50% methane (CH_4), and greater than 75% of nitrous oxide (N_2O) emitted annually by human activities (Tubiello et al., 2007). In the EU, for example, agriculture contributed CH_4 and N_2O emissions equivalent to 383 Mt carbon dioxide (CO_2) equivalents in 2000, corresponding to approximately 10% of the total EU GHG emissions (Weiske et al., 2006). Oenema at al. (2007) conceptualises possible loss pathways of nutrient elements from the feed – animal – manure – soil – crop chain (Fig. 1.3), with losses decreasing in the order: C, nitrogen (N) >> sulphur (S) > potassium (K), sodium (Na), chlorine (Cl), boron (B) > phosphorus (P), calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), copper (Cu), molybdenum (Mo), cobalt (Co), selenium (Se), nickel (Ni). Carbon is released from manure in gaseous forms (mainly as CO_2 and CH_4), in dissolved forms as inorganic and organic C [(bicarbonate (HCO_3) and dissolved organic carbon (DOC)], and as particulate matter via runoff. Nitrogen is also released in gaseous forms [mainly as ammonia (NH_3), atmospheric nitrogen (N_2), N_2O, and nitric oxide (NO)], in dissolved forms as inorganic and organic N [nitrate (NO_3), ammonium (NH_4) and dissolved organic nitrogen (DON)], and as particulate matter via runoff.

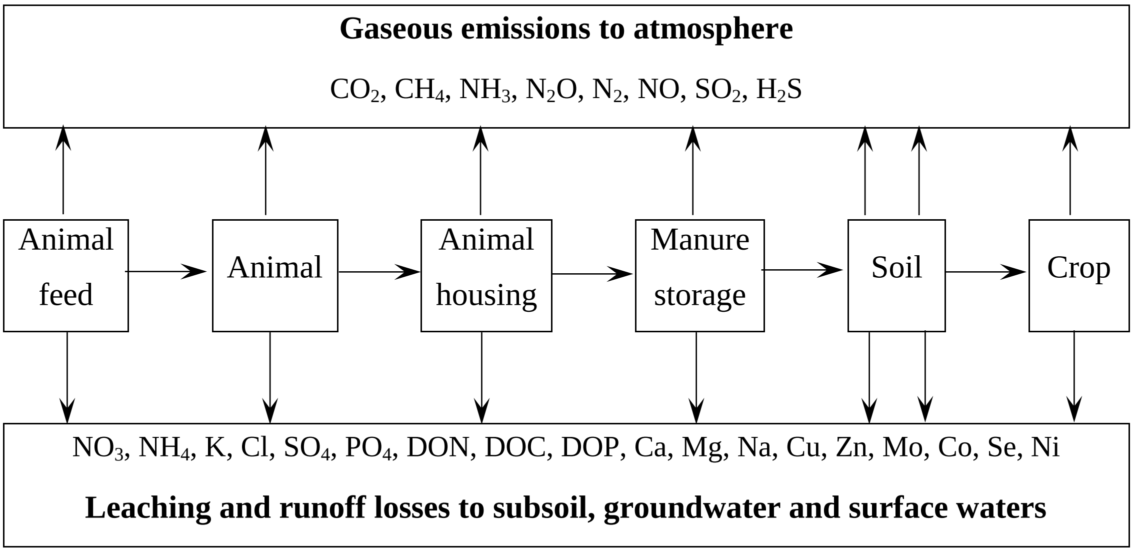

Figure 1.3 Possible loss pathways of nutrient elements from the feed – animal – manure – soil – crop chain (Oenema et al., 2007)

Potassium, Na, Cl and B have high solubility in water, and their main loss pathway is via leaching. The elements P, Ca, Mg, Fe, Mn, Cu, Zn, Mo, Co, Se and Ni have low mobility because of their low solubility and high reactivity with soil constituents (Sparks, 2003). Current environmental concerns from manure management systems relate mainly to gaseous emissions of NH_3, N_2O and CH_4 to the atmosphere and leaching of NO_3 to groundwater and inorganic N (NO_3, NH_4) and P [ortho-phosphorus (PO_4)] to surface waters.

1.2 Impact of agriculture on water quality

Ground and surface water quality is adversely impacted by agricultural activities via a number of pathways, including soil erosion (Creamer et al., 2010), N and phosphorus (P) losses in surface runoff (Preedy et al., 2001) and leaching (Kleinman et al., 2009; Ulén et al., 2013; Fenton et al., 2017), leaching of pathogenic and harmful slurry-borne contaminants such as animal husbandry-derived antimicrobials and hormones (Gerba and Smith, 2005; Lee et al., 2007), increased faecal indicator organisms through application of organic fertilizers (Hodgson et al. 2016), and persistent use of chemical and pharmaceutical products such as pesticides and herbicides (Cerar and Mali, 2016). In inland waters, P from agricultural activities is a major contributor to accelerated eutrophication. For example, most of the largest lakes in Latin America and Africa have increasing P loads arising from anthropogenic activities while severe pathogen pollution already affects around one-third of all river stretches in Latin America, Africa and Asia. The number of people at risk to health by coming into contact with polluted surface waters may range into the hundreds of millions on these continents (UNEP, 2016). Severe organic pollution already affects around one-seventh of all river stretches in Latin America, Africa and Asia, and is of concern to the state of the freshwater fishery and its importance to food security and livelihood (UNEP, 2016).

In Ireland, approximately 13,200 km of river channel and 213 lakes are assessed for quality on an ongoing basis by the Environmental Protection Agency (EPA) at 2,300 sample stations. The latest EPA report (period 2010 – 2012) found that while 53% of rivers and 43% of lakes were satisfactory at good or high status, eutrophication remains the most significant issue for surface waters, with agriculture and municipal sources accounting for 53% and 34% of river pollution (Bradley et al., 2015). A total of 336 groundwater sites, covering an area of approx. 69,000 km^2, were also monitored, and the report found that the south and south-east of the country continue to have the greatest proportion of groundwater and rivers with nitrogen (N) concentrations over 10 mg NO_3 L^{-1} (Bradley et al., 2015).

The agronomic (Teshager et al., 2016), ecological (Heffernan et al., 2014) and health (Carmichael and Boyer, 2016) implications of deteriorating water quality are therefore of national and global concern (Zhang et al., 2015; Qui, 2010) and in order to meet growing food demand, environmentally sustainable, economically viable and productive farming systems are required against the background of greater competition for land, water and energy (Godfray et al., 2010). The challenge, therefore, is to produce more food from the same area of land while reducing the environmental impacts and this requires sustainable intensification (Baulcombe et al., 2009). In the studies included in this thesis, the abatement of C, N, P and suspended solid (SS) losses in surface runoff, losses of C, N and P in soil leaching, and CO_2 and CH_4 emissions from land applied dairy and pig slurries and dairy soiled water (DSW) have been investigated. Passive filtration methods to treat DSW using sand and woodchip filters have also been examined.

1.3 Nutrient loss pathways during land application of agricultural manures

Agricultural management has been identified as a landscape pressure impacting on water quality (Sharpley et al., 2001; Kronvang et al., 2005; Schulte et al., 2006), where transfers of N, P and C may lead to eutrophication and elevated levels of dissolved organic C and groundwater contamination. These transfers occur as (i) chronic losses, where nutrients in excess of crop requirements build up in the soil, (ii) incidental or event losses as a result of direct transfer of manures to water during land application, or where a rainfall event occurs immediately after application and (iii) leaching losses. Gaseous losses of N_2O, CO_2 and CH_4 from agricultural activity also contribute significantly to anthropogenic GHG emissions. The frequency and timing of rainfall following application of manures or fertilizers have been shown to affect runoff losses. For example, Sharpley (1997) observed that N and P concentrations in runoff from soils fertilized with poultry litter reduced after successive rainfall events, and when the interval between rainfall and manure application was increased. Storm hydrology also has a significant impact on manure losses in runoff, with larger losses from more intense rainfall even after intervals up to 30 d between manure application and rainfall events (Vadas et al, 2011).

1.3.1 Nitrogen

The earth's atmosphere, which is the ultimate source of all soil N, consists of 78% N and undergoes many transformations (Fig. 1.4). Manure N comes in both organic and inorganic forms. Inorganic N, mostly NH_4 and NO_3, is readily available to plants. Organic N comprises over 95% of the N found in soil and cannot generally be used by plants. It is gradually transformed (mineralised) by soil microorganisms to NH_4 and not leached to a great extent. Since NH_4 is a positively charged ion (cation), it is attracted to and held by the negatively charged soil clay. In temperate, well-drained soil, NH_4 is oxidised rapidly to NO_3 by two groups of chemo-autotrophic bacteria [ammonium oxidising bacteria (AOB) and nitrite oxidising bacteria (NOB)], which operate in sequence as represented by Equations 1 [transformation of NH_4 to nitrite (NO_2)] and 2 (transformation of NO_2 to NO_3).

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 4H^+ + 2H_2O \qquad (1)$$

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2NO_3^- \qquad (2)$$

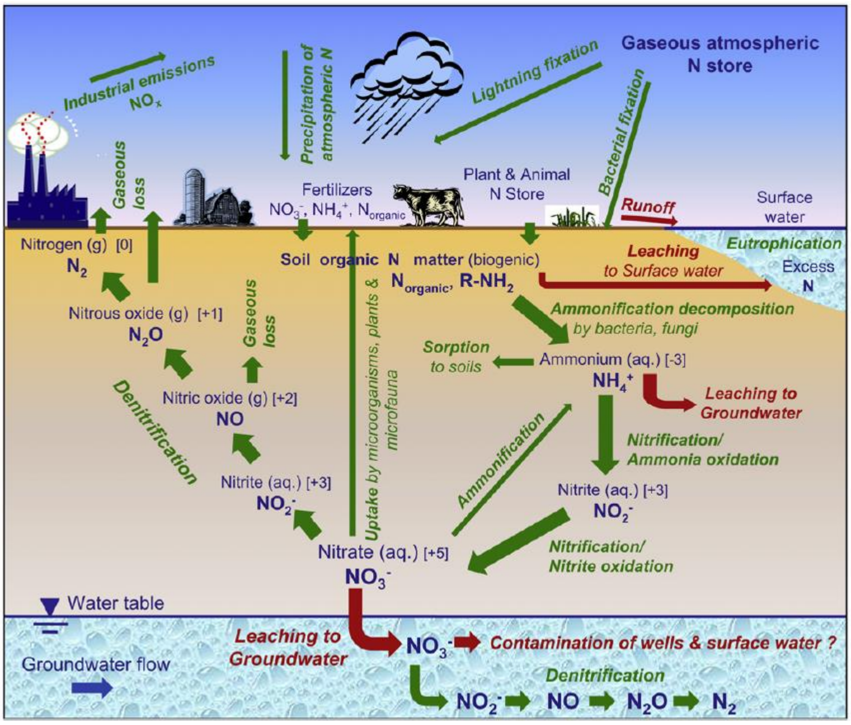

Figure 1.4 The nitrogen cycle and its influence on the water and air environment (Rivett et al., 2008).

Nitrate is the principle form of N used by plants but leaches easily, since it is a negatively charged ion (anion) and is not attracted to soil. It is therefore a major source of groundwater pollution, particularly in sandy or shallow soils. When soil does not have sufficient air, microorganisms use the oxygen from NO_3 in place of that in the air and rapidly convert NO_3 to nitrogen oxide and nitrogen gases (N_2) via the process of denitrification. These gases escape to the atmosphere and are therefore not available to plants. This transformation can occur rapidly, depending on factors such as pH, temperature and water content of the soil, and may result in large losses from nitrate rich fertilizers. Nitrification and denitrification are important process when treating wastewaters (e.g. DSW) and the primary objective is to reduce N loads in the wastewater by transforming organic and inorganic N to N_2 gas. Nitrification is sensitive to environmental influences such as temperature, C:N ratio, pH and toxicity, while denitrification requires an anoxic zone and sufficient available carbon. Soils that have a high pH (>9.5) can also lose large amounts of NH_4 by conversion to NH_3 gas, termed ammonia volatilization.

1.3.2 Phosphorus

Phosphorus is an essential crop macronutrient, but the challenge of supplying adequate P for economic agricultural production while minimising losses to surface water is a difficult one due to the very low P concentrations (as low as 10 $\mu g\ L^{-1}$) that can cause eutrophic and hypereutrophic conditions (Haygarth et al., 1998; Sharpley et al., 2001). Such conditions lead to low oxygen levels, reduced aquatic species diversity, turbidity, and undesirable taste and odour in potable water supplies (Zaimes and Schultz, 2002). In 2002, the World Health Organisation (WHO, 2002) reported that when P is the limiting factor (i.e. if N:P is greater than 16:1 in the water body), a phosphate concentration of 0.01 mg L^{-1} is enough to support plankton, and concentrations from 0.03 to 0.1 mg L^{-1}, or higher, are likely to promote algal blooms. A large proportion (up to 90%) of P exported from catchments on an annual basis may be generated from a relatively small portion of the catchment and during only one or two storm events (Sharpley and Rekolainen, 1997). Soil P is found in various chemical and physical forms which differ in their plant availability and environmental fate. Zaimes and Schultz (2002) describes the soil P cycle (Fig. 1.5), which includes inputs and outputs as well as internal cycling of P. A point to note about the soil P-cycle is that there is no process to remove P to the atmosphere like in the N-cycle. The major internal P inputs are weathering and the major external P inputs to soil include fertilizers, agricultural wastes, plant residues, atmospheric deposition, and municipal/industrial by-products. The internal cycling processes include immobilization-mineralization, adsorption-desorption, and precipitation-dissolution.

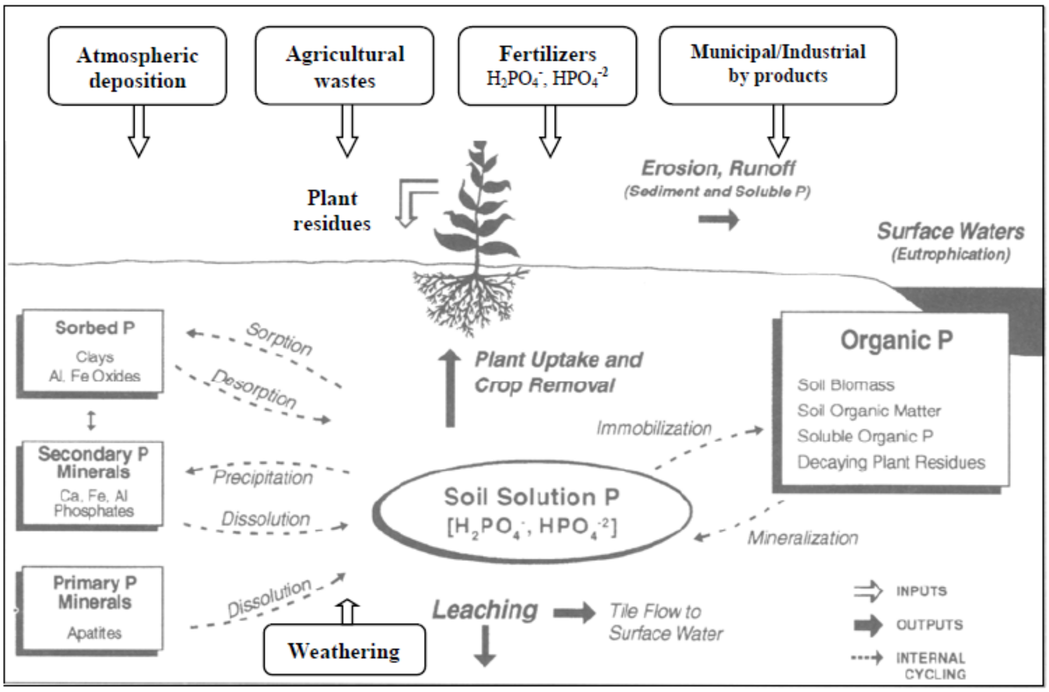

Figure 1.5 Phosphorus cycle in the soil (Zaines and Schultz, 2002)

Hansen et al. (2002) simplifies the P cycle by describing three hypothetical pools of soluble P, reactive P and stable P (Fig. 1.6). The soluble pool is the smallest and most plant available and is predominantly in the form of PO_4. The reactive and stable pools are in organic and inorganic forms, and are in dynamic equilibrium with the soluble P pool. The organic P in the reactive pool is from relatively fresh organic material that is readily decomposed. When soluble P uptake or loss occurs, P from the reactive pool can replace it through processes such as desorption, dissolution and mineralisation. Stable P forms are in equilibrium with the other pools, but the reactions of stable P pools are too slow for time periods important in agricultural production. The soil test phosphorus (STP) measurement methods (e.g. Bray-I, Olsen, and Mehlich-I and –III) were designed to provide an estimate of the amount of soil P that would be available to a crop during the growing season i.e. the soluble and reactive pools (Neyroud and Lischer, 2003).

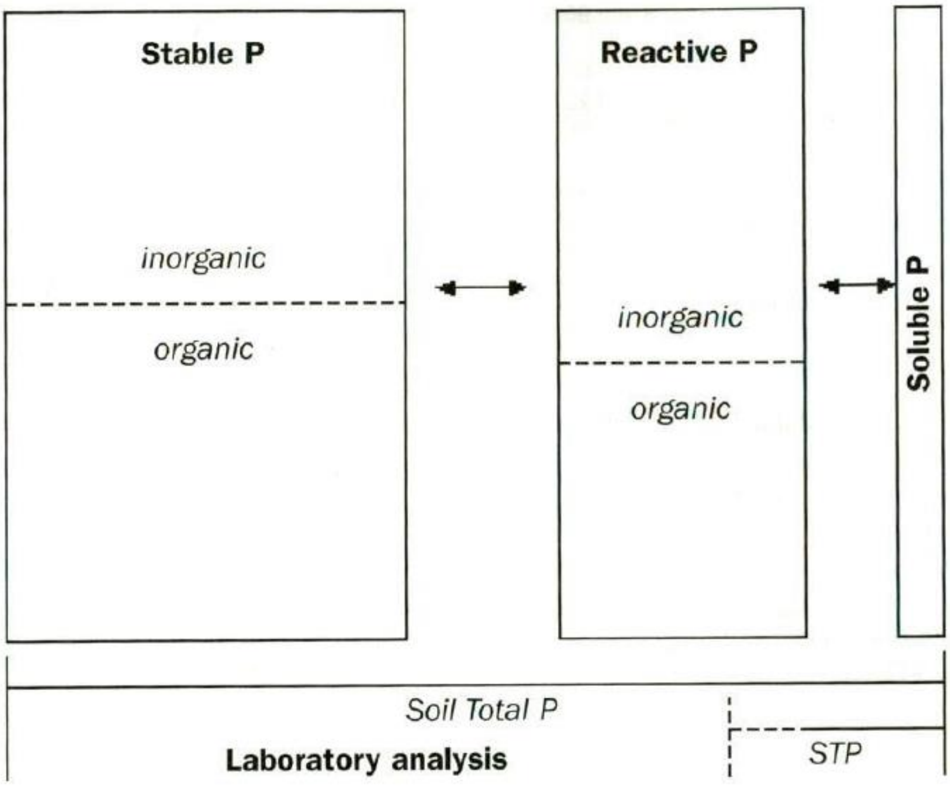

Figure 1.6 Illustration of the interrelationships between the three pools of soil phosphorus and their relationship to the soil test phosphorus (STP) analyses which estimate the amount of soil P that would be available to a crop during the growing season (Hansen et al., 2002).

Transport of P in the terrestrial environment occurs by mobilisation from its source and includes chemical, biological and physical processes (Fig. 1.7). The hydrological pathways of P movement from fields include surface runoff comprising overland flow, and subsurface flow comprising preferential flow, interflow, leaching and drainflow (Nasr et al., 2006). Soluble P (<0.45 μm) in runoff originates from a thin zone of surface soil (1 – 2.5 cm) with a high STP resulting from long term addition of manure or fertilizer in excess of crop requirements. Particulate (suspended or sediment-bound) P (>0.45 μm) is associated with soil and vegetative material eroded during runoff, and in most cases is typically the dominant form of P lost (Sharpley et al., 1995; Fang et al., 2002).

Although leaching is generally thought to be of little concern when compared to surface runoff (Haygarth et al., 1998; Algoazany et al., 2007), accumulated P may be lost from the soil through downward leaching to groundwater, either by slow leaching through the soil profile or preferential flow through macropores (Sims et al., 1998; Koopmans et al., 2007). The sorption capacities of the soil, the potential for P release from the soil, and the pathways for preferential flow within the soil structure are the most important factors which may contribute to P leaching loss from soil receiving P fertilisation (Djodjic et al., 2004). Preferential flow is the main transport mechanism for P leaching in fine-textured soils (Djodjic et al., 2004; van Es et al., 2004), while P sorption capacity is generally the most important factor for P leaching in slow draining soils (Djodjic et al., 2004). When the P sorption capacity of soils becomes exhausted, the risks of P leaching to groundwater increases (Sims et al., 1998).

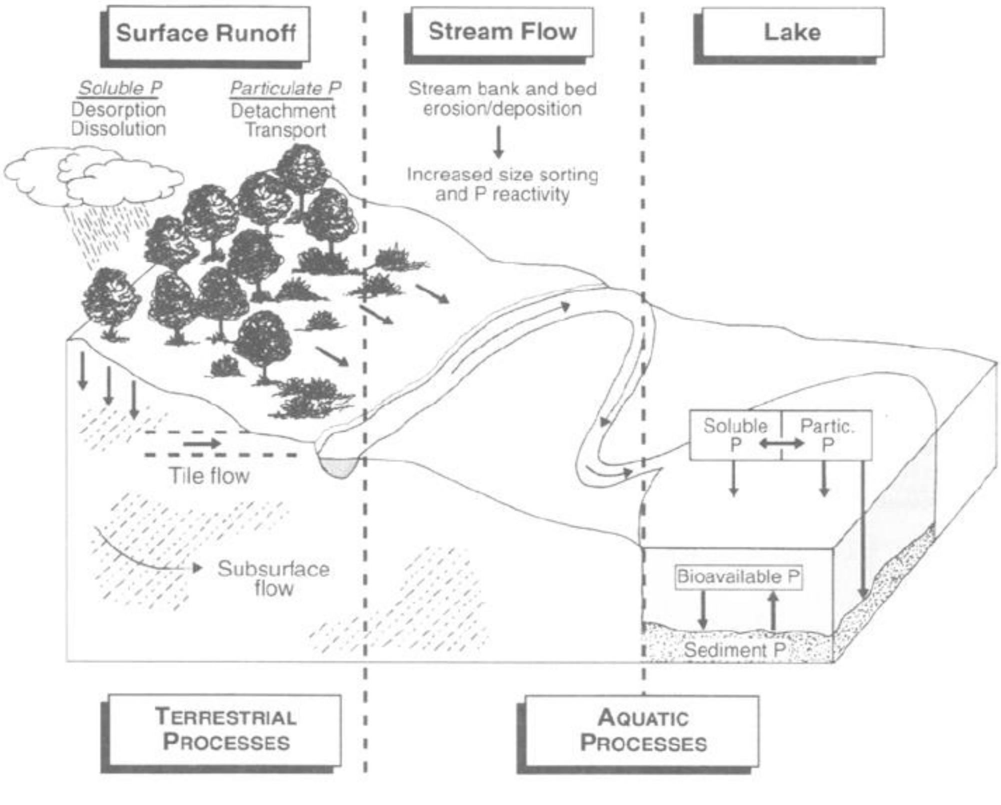

Figure 1.7 Processes in the transfer of P from terrestrial to aquatic ecosystems (Pierzynski et al., 2000).

Incidental or event-specific transfer of dissolved and particulate phosphorus (PP) to surface waters may occur when fertiliser or manure applications, which are not incorporated into the soil, are coincident with onset of rainfall (Haygarth and Jarvis 1999). The relative proportions of PP and dissolved P in surface runoff, therefore, depend on the complex interaction between climate, topography, soil type, soil P content, type of farming system, and farm management (Withers, 1999). The application of manures to soil has been shown to significantly decrease the P sorption maxima of the soil (Siddique and Robinson, 2003). Unlike most dissolved reactive phosphorus (DRP), which is readily available for plant uptake, PP acts as a long-term source of P for submerged aquatic vegetation and algal growth (Sharpley, 1993; Søndergaard et al., 2001), particularly in shallow lakes where inflowing rivers deposit nutrient-enriched sediment on the lake floor.

1.3.3 Carbon

The global soil C pool of 2,500 gigatonnes (Gt) includes about 1,550 Gt of soil organic carbon (SOC) and 950 Gt of soil inorganic carbon (SIC) (Lal, 2004a). The soil C pool is between two and four times greater than the atmospheric pool (Fig. 1.8) and about four times greater than the C stored in plants, and is therefore viewed as a C sink that potentially has a significant impact on sequestering CO_2 emissions. For example, Paustian et al. (1997) estimate that the capacity for C sequestration in agricultural soils globally are in the order of 20 – 30 Pg C over the next 50 – 100 years. *(1Pg = 1Gt =*10^{12}*kg =* 10^9 *tonnes).*

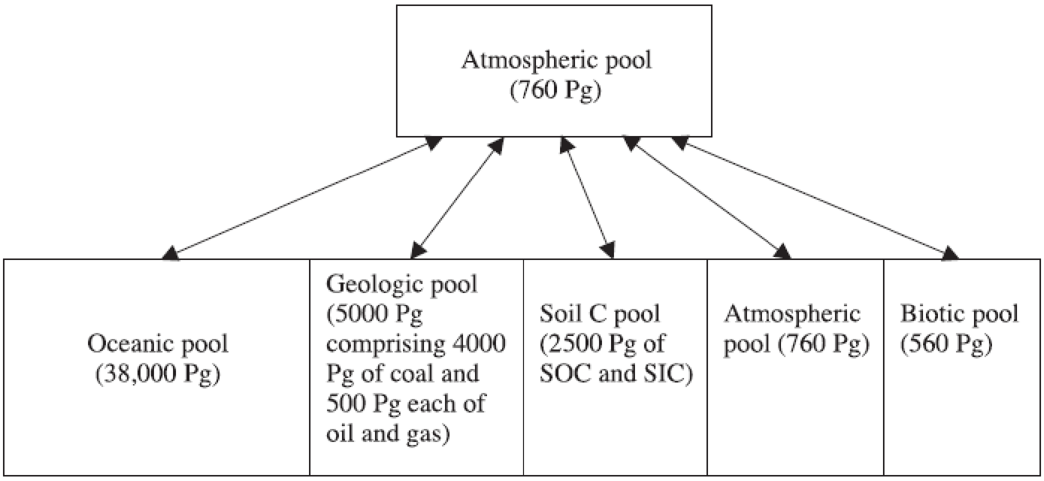

Figure 1.8 Principal global carbon pools (Lal 2004b).

Inorganic soil C is generally found as carbonates of calcium ($CaCO_3$, or limestone) and magnesium ($MgCO_3$). The organic forms of C in soil are a very diverse group of materials that are of biological origin and include live plant roots and litter, humus, charcoal and other recalcitrant residues of organic matter decomposition. Organic C also includes organisms that live in the soil, collectively called soil biota (e.g., fungi, bacteria, mites, earthworms, ants and centipedes). Because all these materials contain C, the terms soil organic matter (SOM) and SOC are often used interchangeably; on average, SOM contains 58 - 60% C by weight. While application of organic manures provide several advantages such as improving plant growth and yield, soil C content, microbial biomass activity and improving soil structure and fertility, it also possesses some disadvantages such as eutrophication from nutrient losses and GHG emissions of CO_2, CH_4 and N_2O (Fig. 1.9).

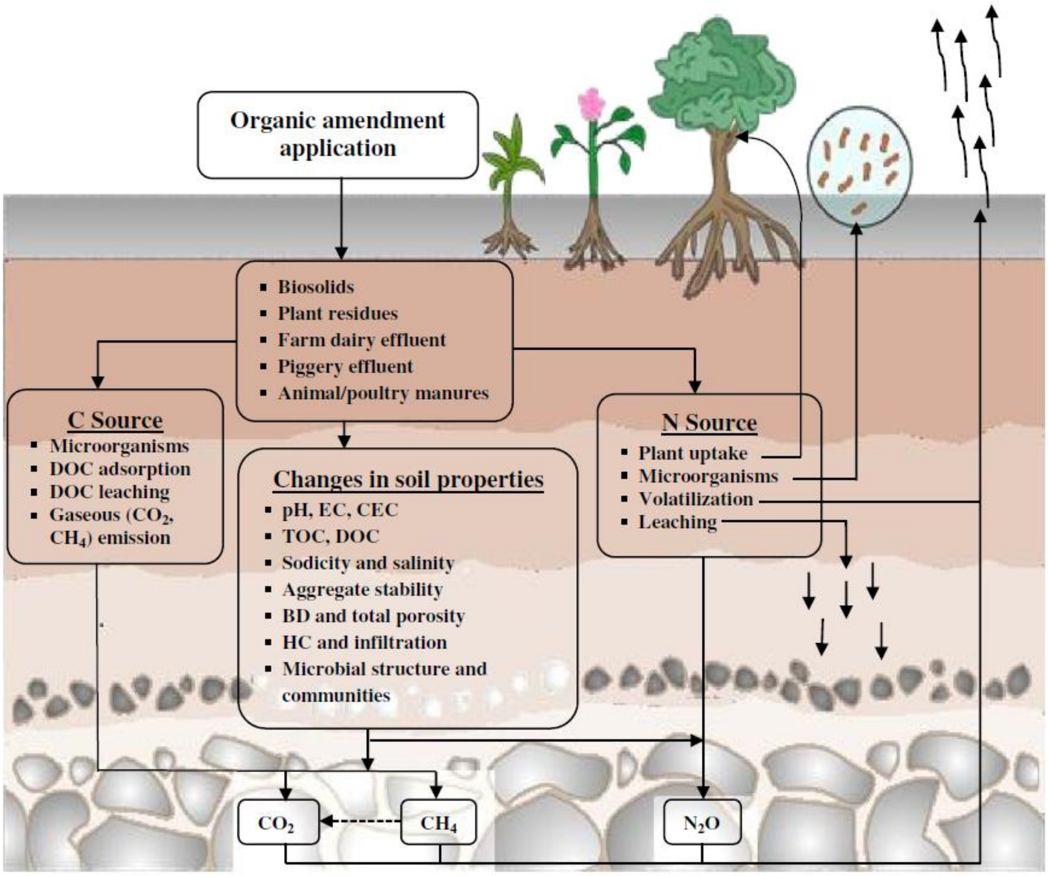

Figure 1.9 Schematic representation of the effect of organic amendments acting as a source of C and N and altering soil properties affecting greenhouse gas emissions (CO_2, CH_4 and N_2O) (Thangarajan et al., 2013).

Soil organic matter can be categorised in four major pools which vary in their chemical composition, stage of decomposition, and role in soil functioning and health: (i) crop and root residues, which are broken down relatively quickly (weeks to years), and provide an important source of energy for soil microorganisms (ii) particulate organic C or ‘labile’ C is defined as plant debris 0.053 - 2 mm in size, which decomposes relatively quickly (years to decades) and provides an important source of energy for soil microorganisms. It also plays an important role in maintaining soil structure and providing soil nutrients (iii) humus, which consists of decomposed material less than 0.053 mm in size, and is usually found attached to soil minerals. This type of carbon is more resistant to decomposition by soil microorganisms, and so tends to turn over more slowly (over decades to centuries). It plays a role in all key soil functions, and is particularly important in the provision of nutrients (iv) recalcitrant organic carbon is resistant to decomposition and can take centuries to thousands of years to decompose, and is largely unavailable to microorganisms (Bell and Lawrence, 2009; Hazelton and Murphy, 2016).

The amount of labile carbon influences both the activity and mass of microorganisms (microbial biomass) in soil. However, the capacity of these microorganisms to release plant nutrients, such as N, is influenced by the quality of organic matter inputs. Soil microorganisms need nutrients to grow and if the plant residues added to soil contains large amounts of C (stimulating soil microbial growth), but low amounts of nutrients, such as N, then soil microbes will need to use all the nutrients contained within organic matter for their own growth. They may even take up nutrients from the soil, tying it up temporarily in the microbial biomass (immobilization). If plant residues contain more nutrients than are required by soil microbes, the excess will be released into the soil and be available for plants. Net release of N, for example, usually occurs when the plant residues added to soil have a C:N ratio less than 22:1. As soil organic material decomposes, there is generally more C consumed by soil microorganisms than there are nutrients released. As a result, soil organic materials become increasingly nutrient-rich as decomposition occurs. Cereal straw, for example, is made up of C and N in the ratio of 100:1 when it is added to the soil. As this material decomposes and forms humus, it’s C to N ratio decreases to 12:1. Consequently, while humus is more resistant to decomposition than the more labile fractions, it is nutrient-rich and is a valuable source of nutrients contributing to soil fertility (Stine and Weil, 2002; Hoyle and Murphy, 2006; Hoyle at al., 2011).

The capacity of soils to store C is influenced by soil type (clay content, bulk density, depth and mineralogy), climate (rainfall, temperature and solar radiation) as well as management (plant productivity, rotation strategy and soil management) (Ingram and Fernandes, 2001). Clay particles and aggregates can reduce losses of SOC by physically protecting organic matter from decomposition. Particles of organic matter can become adsorbed to clay surfaces, coated with clay particles, or buried inside small pores or aggregates. These processes make it difficult for microorganisms to come in contact with organic matter and, therefore, the amount of SOC stored tends to increase with increasing clay content. In contrast, in sandy soils, which usually are more aerobic than clay soils, microorganisms are able to more easily access SOC and this causes greater decomposition losses. Rainfall is the climate factor that has most influence on plant productivity and, therefore, inputs of SOC. In regions with high rainfall, soils tend to have greater attainable storage of SOC than the same soil type in a lower rainfall region. Management practices determine the actual storage of SOC by increasing inputs and decreasing losses. For example, improving soil structure can increase the amount of SOC stored by reducing losses of SOC by decomposition and erosion, e.g. retaining stubble, maintaining ground cover, and reducing compaction by vehicles and stock. In a review of critical levels of SOC in tillage land in Ireland, Spink et al. (2010) concluded that soil function is unlikely to be adversely affected when SOC is above a threshold of 2% (equivalent to *c.* 3.4% SOM). Therefore, soils with less SOM than this should be further assessed to see if they are in good environmental and agronomic condition. On the other hand, excessive amounts of SOC in soils may result in increased losses of dissolved organic carbon (DOC) to surface waters, which if abstracted for potable water treatment, may affect the functioning and cost of treatment e.g. coagulation, oxidation, adsorption, and membrane filtration. While SOC is not toxic of itself, it can transport contaminants and toxic compounds, and is a precursor of harmful disinfection by-products, in particular trihalomethanes (THMs) (Seekell et al., 2015).

1.4 Legislation

There is extensive worldwide legislation for the prevention and control of water pollution. For example, the Clean Water Act (CWA) establishes the basic structure for regulating discharges of pollutants into the waters of the U.S. and regulating quality standards for surface waters. In the EU, the Water Framework Directive (EU WFD) was adopted in 2000 with the aim of protecting all waters including surface, ground and coastal waters, and achieving "good status" for all waters by 2015

(European Commission, 2000). The WFD was implemented through national environmental regulations by Member States. The programme of measures (POM) adopted by the agricultural sector Ireland is included in Statutory Instrument (SI) No. 31 of 2014 and incorporates the requirements of both the WFD and the Nitrates Directive (EEC, 1991) (European Commission, 1991). The Nitrates Directive, implemented in 2009, aims to protect European water quality through the use of good farming practices which prevent excessive nutrients from agricultural sources polluting ground and surface waters. Guidelines for farm management include best practice for collection and management of slurry storage facilities, and application of organic and inorganic fertilizers, including DSW, to grasslands. For example, landspreading of slurries are prohibited during a winter closed period (15th October to 15th – 31st January). Slurry spreading is also prohibited when heavy rainfall is forecast within 48 h of application to allow for increased interaction time between slurry and soil before rainfall in order to minimise nutrient losses in runoff to waterbodies. The limits on the permissible amounts of livestock manure that can be applied to land, as set out in article 20 of the SI, are 170 kg N and 41 kg P ha^{-1} yr^{-1}, but are also dependent on grassland stocking rates and STP (based on Morgan's P). The P indexing system is based on four categories (Schulte et al., 2010) ranging from 1 (deficient soil P, insignificant risk of P loss to water) to 4 (excess soil P status, high risk of loss to water).

SI No. 31 of 2014 defines DSW as wash water from livestock, silage effluent, chemical fertilisers, vegetables, milking parlours, mushroom houses, and farm equipment which has a dry matter (DM) content <1% and a biochemical oxygen demand (BOD) <2,500 mg L^{-1}. The limit of DSW application to land is 50,000 L ha^{-1} in any 42-day period or an irrigation rate of less than 5 mm h^{-1} and reduce to 25,000 L ha^{-1} in any 42-day period or 3 mm h^{-1} in karst limestone aquifer areas. The management and disposal of DSW, which is perceived to be of little or no agronomic benefit, is of particular concern to farmers as it requires 10 – 15 days storage capacity and is both costly and difficult to dispose of, particularly during winter periods when land cannot be easily travelled by landspreading equipment. Treatment and disposal of DSW, therefore, remains a high priority for research in the agricultural sector.

1.5 Options for treatment and disposal of agricultural slurries

The failure of many countries, including Ireland (Wall et al., 2016), to meet EU WFD targets of improved water quality is a common throughout Europe. Indeed, the failure is not unique to Europe, and it is largely accepted that supplementary measures will be critical to develop short term farm management practices, which will reduce nutrient losses, in particular P losses, to waterbodies (Buda et al., 2012). While it is acknowledged that the impacts of many farm management practices to reduce nutrient emissions may take a long time, perhaps years (e.g. Huebsch et al., 2013), these alone may not be sufficient and additional measures or 'new tools' (Buda et al., 2012) are also required to prevent acute losses, in particular P losses. Current farm management practices to reduce nutrient losses include incorporating slurry into soil (e.g. incorporated after tillage) (Tabbara, 2003; Kayser et al., 2015), increasing length of buffer zones between slurry application areas and drains and streams (Mayer et al, 2005), enhanced buffers strips (Uusi-Kämppä et al., 2000), timing of slurry application (Hanrahan et al., 2009), application of chemical amendments (Dou et al., 2003; Brennan et al., 2011; Brennan et al., 2014) and diet manipulation (O'Rourke et al., 2010). Mitigation methods to reduce NH_3 and N_2O emissions include addition of amendments (Lefcourt and Meisinger, 2001), nitrification inhibitors (Ruser and Schulz, 2015), acidification (Fangueiro et al., 2015), and slurry application techniques (Figure 1.10).

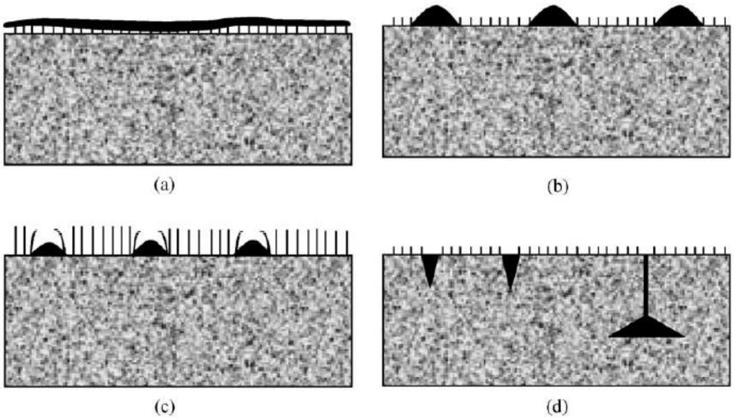

Figure 1.10 Schematic representation of slurry applied to soil using different application techniques: (a) surface application – uniform covering of slurry across the crop (b) band spreading - slurry placed in discrete bands on the crop by trailing hoses (c) trailing shoe - slurry placed in discrete bands on the soil surface below the crop canopy (d) injection - slurry placed in shallow, open slots or deep, closed slots within the soil (Misselbrook et al., 2002).

In the following sections, alternative technologies to landspreading of livestock wastes and land management are discussed and contextualised.

1.5.1 Slurry separation

Slurry separation results in separate liquid and solid fractions, which are then treated separately. A key aim of solid-liquid separation is to reduce transport costs of the solid fraction to available lands (e.g. crop producing lands) by increasing its DM and consequently its fertilizer value. Separation may also contribute to a reduction in odour emission (Zhang and Westerman, 1997) and assist in producing energy-rich biomass that can be used for incineration or biogas production (Møller et al., 2007a; Hjorth et al., 2009). Solid-liquid separation may be carried out in settling or thickening tanks, or in mechanical separators such as centrifuge, belt press, or screw press. Slurry thickening tanks are a low-cost option for separation using simple technology [Fig. 1.11 (A)]. Slurry is added to the top of the thickener and the solids settle to the bottom, aided by a mechanically rotating picket fence (Loughrin et al., 2006). Thickeners have been found to be most effective for slurries in the range 1 - 2% DM and least effective for slurries with DM >5% and < 0.5% (Hjorth et al., 2010). Centrifugation operates by applying a centrifugal force, which separates solids and liquids at the wall into an inner layer with a high DM concentration and an outer layer consisting of a liquid containing a suspension of colloids, organic components and salts [Fig. 1.11 (B)]. Typically, centrifuged slurries have a DM of 18 – 20%, depending on the type of slurry applied. There are many types of belt and screw or auger presses commercially available, and these use screens and filter belts to retain the solid fractions. The slurry is fed onto the unit, where it is squeezed between permeable belts or screw compacted and the solids are then removed using a scraper, while the liquid (filtrate) flows through the screen or belt. With a belt separator, the filter cake is continuously removed as the belt rotates, so that the raw-slurry loading area and solid-fraction unloading area change over and are cleaned continuously [Fig. 1.11 (C)]. Typical DM of the solid fraction of slurries after thickening by belt press also lie in the range 18 – 20%.

Figure 1.11 Slurry separation using thickening tank with rotating picket fence thickener (A); centrifuge (B) and belt press (C).

1.5.2 Treatment of solid slurry fraction

Following separation, solid slurry fractions are generally treated by composting, anaerobic digestion (AD), and more recently by use as biochar.

1.5.2.1 Composting

Composting is a process in which organic material undergoes biological degradation to a stable end product, which is generally used as a soil conditioner in agricultural or horticultural applications. Approximately 20 – 30% of the volatile solids are converted to CO_2 and water in the composting process. As the organic material in the slurry decomposes, the compost heats to temperatures in the pasteurisation range (50 – 70 °C) and enteric pathogenic organisms are destroyed (Larney and Hao, 2007). Most composting operations consist of the following basic steps: (i) mixing the solid fraction of slurry with an amendment or bulking agent. Commonly used amendments are sawdust, straw, recycled compost and rice hulls, which provide structural support and increase the porosity of the mixture for effective aeration (Tchobanoglous and Burton, 1991) (ii) aerating the compost pile either by the addition of air, or by mechanical turning, or by both (iii) recovery of the bulking agent, where possible (iv) further curing and storage, and (iv) final disposal. The three major types of composting systems used are aerated static piles and aerated windrows (Fig. 1.12). Windrows are ideally operated at C:N ratios in the range 20 – 25:1 and a moisture content of 50 – 60%. If the C:N ratio falls below this, NH_3 gas and odours may be released, and if the ratio is greater, the microorganism activity will be reduced, leading to slower decomposition rates (Zhou, 2016).

Figure 1.12 Windrow composting system (source windrow systems) (accessed Feb. 2017).

1.5.2.2 Anaerobic digestion

In the anaerobic digestion process, the slurry (or co-digested slurry) is converted biologically, under anaerobic and mesophilic (30 – 38 °C) conditions, to a variety of end products including CH_4, which can be used for both heat and power generation and CO_2. Slurry is introduced continuously or intermittently and retained in the reactor for varying periods of time, typically 30 – 60 days. The stabilised sludge (digestate), withdrawn continuously or intermittently from the reactor, is reduced in organic and pathogen content, and is non-putrescible. The residue of AD, called digestate, can be used as a fertilizer and has enhanced nutrient availability and increased flow characteristics (Ward et al., 2008).

Anaerobic digestion of manures is already a widely used technology on mainland Europe, especially in Germany, Denmark, Austria and Sweden (Holm-Nielsen et al., 2009). There are two models used for AD of manure in these countries: farm-scale units and centralised plants (Holm-Nielsen et al., 2009). In Germany, there are more than 4,000 on-farm AD units (Wilkinson, 2011). The German government intends to increase this number to between 10,000 and 12,000 by 2020 to meet renewable energy targets (Wilkinson, 2011). In Denmark, there are 21 large-scale centralised AD systems and 60 farm-scale plants which treat 5% of all manure produced in Denmark. The centralised plants are mostly owned by groups of farmers or co-operatives of farmers and heat consumers. Recent increases in Danish Government incentives are expected to increase the number of centralised plants by around 50, tripling the amount of biogas production by 2025. They aim to process 50% of all animal manures using AD by 2020 (Holm-Nielsen et al., 2009).

Although very attractive as a treatment option, some of the main barriers to the use of AD are the high capital cost necessary for their setup, the low DM content of slurries on many farms which requires separation as an upstream process (Nolan et al., 2012; Møller et al., 2007b), the energy requirement to maintain temperatures sufficient for the digester to operate, and the long residence times required in the reactor. In the long term, however, with improvements in technology and with the support of government initiatives, it is possible that AD may increasingly become a more significant management practice in Ireland and other countries throughout Europe.

1.5.2.3 Biochar

Biochar is a soil amendment with potential to improve N and P recycling in the soil-plant system. Interest in biochar soil applications originally stemmed from the long term fertility of terra preta anthropogenic soils in the Brazilian Amazon. More recently, the recalcitrance of biochar carbon has attracted international attention as an inexpensive and effective way to sequester atmospheric carbon for centuries to millennia, while simultaneously producing carbon-negative energy and improving soil quality (Brewer and Brown, 2012). Biochar is a carbonaceous solid residue produced by heating biomass under oxygen-deficient conditions through slow and fast pyrolysis, gasification and hydrothermal carbonization. The latter three methods are suitable for energy and bio-oil generation at the industrial scale, whereas slow pyrolysis is a traditional method of charcoal production that generates more biochar than the other pyrolysis methods (Brewer and Brown, 2012). The important characteristics of pyrolyzed biochars affecting the biochemical cycling of N and P are high surface area, pH, and nutrient content. These characteristics vary among biochars depending on their source (feedstock) and production temperature. Manure and crop residue-based biochars are richer in nutrients and tend to have higher pH, and greater surface area than the biochars produced from ligno-cellulosic feedstocks such as wood (Gul et al., 2015). Slow pyrolyzed biochars, produced at a high production temperature (≥550 °C), tend to have higher pH values and greater surface area with consequent increased N and P adsorption capacity, but have lower plant-available nutrient concentrations than those produced at a lower production temperature (Al-Wabel et al., 2013). Therefore, for example, low nutrient value biochars (e.g. wood based biochars) with a high surface area will have high N and P adsorption capacities but their application in nutrient poor soils may reduce concentrations of plant available N and P (Cayuela et al., 2013), while biochars produced from manure feedstock are less likely to cause nutrient deficiency in soils (Gul et al., 2015). A conceptual model illustrating the influence of biochar on soil physio-chemical and biological properties with enhanced N and P use efficiency (Fig. 1.13) illustrates the necessity for a comprehensive understanding of biochar-soil interactions to assess the short and long term impacts on soils structure, microbial activity and on crop production.

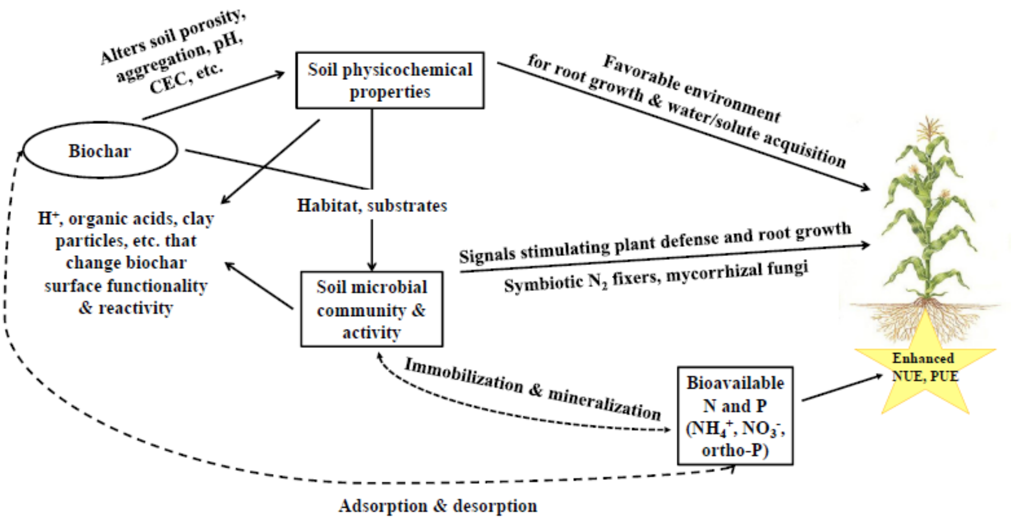

Figure 1.13 Conceptual model illustrating the influence of biochar on soil physico-chemical and biological properties, and the consequences for crop root growth and nutrient acquisition from soil. NUE: nitrogen use efficiency; PUE: phosphorus use efficiency (Gul and Whalen, 2016).

At present, there is inadequate knowledge to develop guidelines on biochar use that are integrated with soil fertility and nutrient management planning (Kwapinski et al., 2010). This is largely due to the fact that an understanding of N and P cycling in biochar-amended soil to date is based on laboratory experiments and therefore field studies are required to determine the magnitude of biochar-induced changes in N and P cycling and to link this to crop performance (Gul and Whalen, 2016).

1.5.3 Treatment of liquid slurry fraction

Following separation, liquid slurry fractions are most commonly treated using either constructed wetlands (CWs) or biological filtration systems.

1.5.3.1 Constructed wetlands

The term *Constructed Wetland* refers to a technology designed to employ ecological processes found in natural wetland ecosystems. These systems utilize wetland plants, soils, and associated microorganisms to remove contaminants from wastewater. Constructed wetlands are complex systems in terms of biology, hydraulics and water chemistry, but are a viable option for the treatment of the liquid fraction of agricultural wastes, including dairy manure, DSW, poultry and pig manure (Knight et al., 2000). Constructed Wetlands generally refers to two types of passive treatment systems. The first and most common type is a free water surface (FWS) constructed wetland, which is a shallow wetland with a combination of emergent aquatic plants (bulrush, reeds, and others), floating plants (duckweed, water hyacinth, and others), and submergent aquatic plants (pondweed, widgeon grass, and others). A FWS CW may have open-water areas dominated by submergent and floating plants and it may contain islands for habitat purposes. The main treatment processes of FWS CWs include sedimentation, as well as biochemical and physical transformations (Fig. 1.14). A second and less common type of system is termed vegetated submerged bed (VSB) or a subsurface flow wetland. Emergent wetland plants are rooted in gravel, but wastewater flows through the gravel and not over the surface. This system is also shallow and contains sufficiently large gravel to permit long-term subsurface flow without clogging. Roots and tubers (rhizomes) of the plants grow into pore spaces in the gravel.

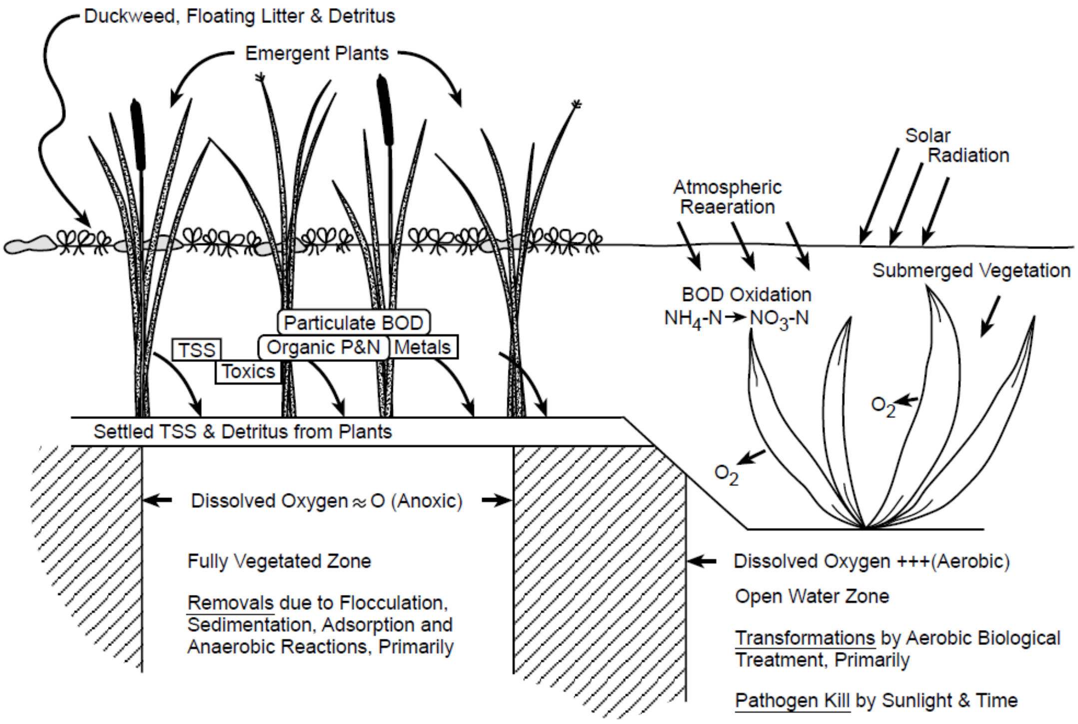

Figure 1.14 Treatment mechanisms that dominate free water surface (FWS) constructed wetland systems (US EPA, 2000).

Treatment efficiencies of CWs are seasonal and are also affected by temperature (Healy and Cawley, 2002; Rozema et al., 2016). An area-based, first order model has become the most widely used to describe CW removal kinetics (Rozema et al., 2016) but because it is difficult to account for variables such as climate variation, pre-treatment control, and time to maturation, conservative design guidelines tend to be used (Healy et al., 2007a). Various surface loading rates are recommended for CWs. For example, American guidelines recommend an areal loading rate of 7.3 g BOD_5 m^{-2} d^{-1}, while New Zealand guidelines for the disposal of farm dairy wastewaters (Tanner and Kloosterman, 1997) recommend that an FWS CW should only be located downstream of two waste stabilization ponds (an anaerobic and an aerobic pond, respectively) and loaded at a maximum organic loading rate of 3 g BOD_5 m^{-2} d^{-1}. A surface loading rate of 5 g BOD_5 m^{-2} d^{-1} has been suggested by Healy et al. (2007a) followed by land application of the treated effluent.

Phosphorus removal from CWs is low as short term (seasonal) P storage is eventually released back into the water due to dieback of algae, microbes and plant residues (unless the plants are harvested), and the only long term P storage is via peat accumulation and substrate fixation, both of which have finite capacity (Healy et al., 2007a). The removal of NH_4 from strong waste waters is generally inadequate in most CWs (Sun et al., 2005; Toet et al., 2005). Inorganic nitrogen removal is also often unsatisfactory (Luederitz et al., 2001) and in Europe, average percentage removal of NH_4 during long term operation is approximately 35%, with a maximum of 50% (Verhoeven and Meuleman, 1999).

Although there is much evidence to support use of CWs, their limitations, particularly with respect to N and P mitigation, the large land usage, susceptibility to weather conditions, and their low rating in terms of cost effectiveness (Nolan et al., 2012), suggests that their widespread use may not be viable in the short to medium term at least.

1.5.3.2 Biological filtration systems

Biological filters are fixed film systems that use a combination of physical, chemical and biological processes to treat wastewater. The microorganisms, which attach to the filter medium, require biodegradable organics, the concentration of which is expressed as either BOD_5, chemical oxygen demand (COD) and total organic C (TOC), as well as nutrients such as N and P, for maintenance and reproduction. The oxidation of soluble organic C is carried out principally by aerobic heterotrophic microorganisms, while conversion of NH_4 to NO_3 via nitrification is carried out by the slower growing and sensitive autotrophic microorganisms. Transformation of NO_3 to N_2 gas via denitrification requires anoxic conditions and sufficient C source (approx. 4 g BOD_5 per g of NO_3-N reduced) (Tchobanoglous and Burton, 1991). Nitrification is affected by a number of environmental factors including pH, temperature, O_2 concentrations, toxins, and the presence of organic carbon. Several studies, for example, have shown that C:N ratio of the applied effluent influences the extent of nitrification in biofilms (Okabe et al., 1996; Nogueria et al., 2002; Wijeyekoon et al., 2004).

Passive treatment systems such as sand filters (Rodgers et al., 2005; Healy et al., 2007b) and woodchip filters (Greenan et al, 2006; Saliling et al, 2007; Ruane et al., 2011; McCarthy et al., 2015) have reported consistently high levels of organic, nutrient and pathogenic removal. Woodchip, in particular, is a cheap, biodegradable material, which has potential use as a soil improver (Cogliastro et al., 2001; Miller and Seastedt, 2009). A laboratory study to compare the effectiveness of intermittently loaded sand and woodchip filters is detailed in Chapter 3 of this thesis.

An on-site filter unit, designed to simultaneously remove COD, N and P from raw DSW, was also constructed on a dairy farm located in an area which formed part of the national Agricultural Catchments Programme (ACP, 2017) in Clonakilty, Co. Cork (south west Ireland). This unit, termed a Permeable Reactive Interceptor (PRI), comprised a sedimentation tank followed by an aerobic woodchip filter and an anaerobic (submerged) zone consisting of alternating woodchip and crushed limestone pockets, and, finally, zeolite as a polishing media (Fig. 1.15). Dairy soiled water was pumped intermittently to the sedimentation tank, from where settled DSW flowed by gravity onto the surface of the aerobic woodchip filter. The filtered effluent then migrated by gravity through the anaerobic zones, before finally discharging to soil. The purpose of the anaerobic zone was to (i) denitrify the nitrified effluent discharging from the aerobic woodchip filter and (ii) remove P by adsorption to the crushed limestone. The zeolite was included to provide a final polishing to the treated effluent and, in particular, to remove any traces of excess N.

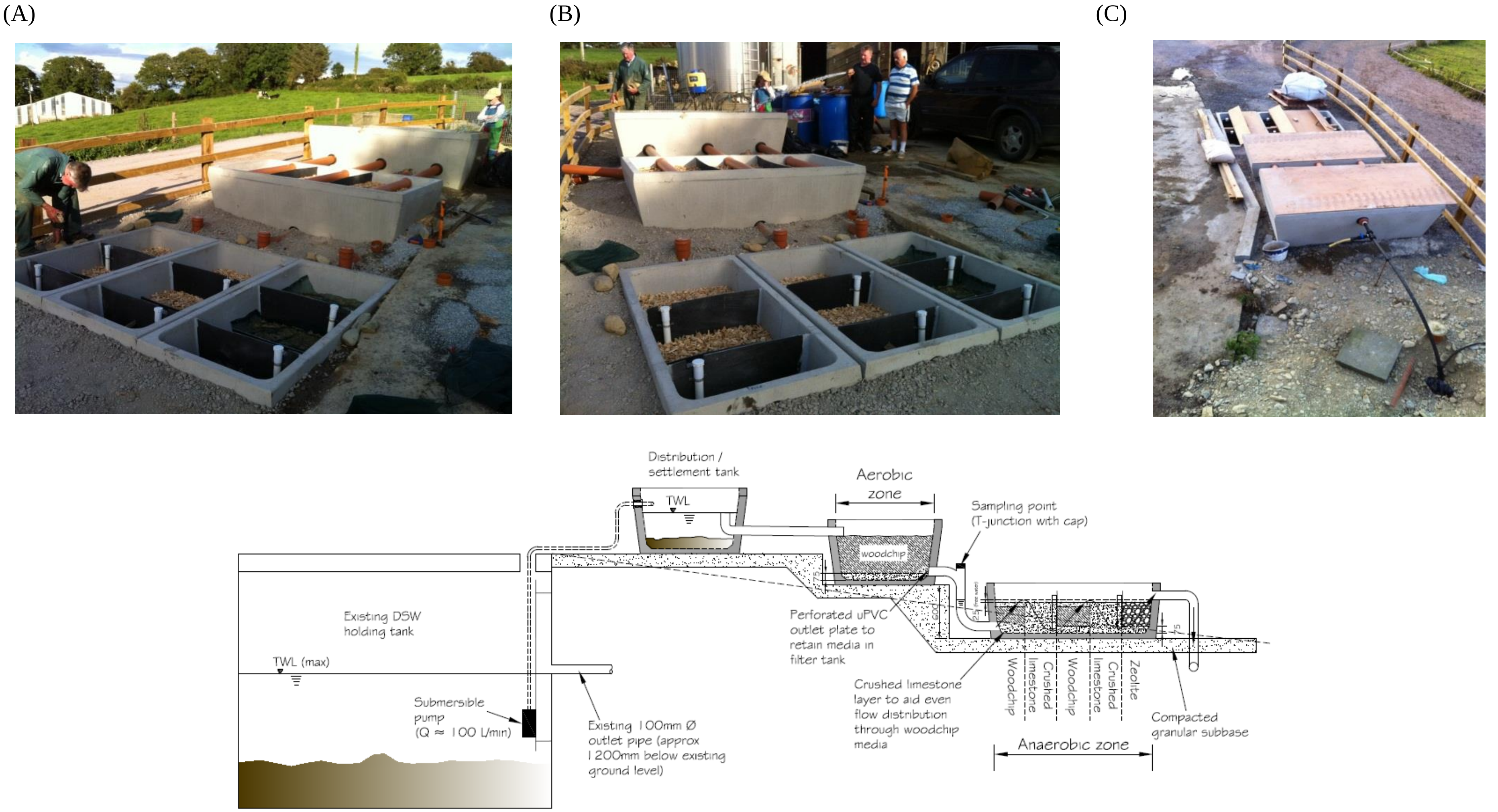

Figure 1.15 On-farm permeable reactive interceptor (PRI), located in the Clonakilty agricultural catchments area, showing completion and testing of the unit (A) and (B); the unit in operation (C) and a schematic section through the unit to illustrate its operation.

The unit had limited success, due mainly to insufficient hydraulic retention time (HRT) (less than 20 min) in the aerobic woodchip filter and concomitant failure to nitrify the influent DSW. In order to improve the operation of the unit, the HRT of the aerobic filter would need to be significantly increased and sufficiently aerated to facilitate nitrification. Possible options to achieve this might be use of a stratified aerobic filter (perhaps woodchip and sand) and/or recirculation of the effluent. While study of this on-site filtration unit does not form part of this thesis, it has nevertheless been described briefly to illustrate attempts to upscale from laboratory to catchment scale studies during the research period.

1.5.4 Soil and slurry amendments

Addition of chemical amendments to soil and to agricultural manures is of increasing interest, particularly in the context of a "circular economy", which seeks to maximise reuse of industrial by-products for the overall benefit of the environment. For example, production of fly ash (FA) and bottom ash (BA) from coal fired power plants has been estimated to exceed 750 million tonnes per annum but less than 50% is utilised (Izquierdo and Querol, 2012). Application of FA with various organic and inorganic amendments to soils has been reported to improve soil quality and lead to higher plant biomass production (Fig. 1.16). More research, however, is needed to develop a greater understanding of the long and short term benefits of blending FA with soils and this may include long term, continuous monitoring of potential contaminants as well as laboratory and field-scale leaching studies (Ram and Masto, 2014). Recently, Herron et al. (2016) reported significant P reductions from a 6 mg P L^{-1} solution using locally sourced red mud and aluminium water treatment residual, and concluded that these by-products may have potential as a low cost P control measure. Soil amelioration using alum sludge has also shown to have beneficial effects (Kim et al., 2002; Moodley and Hughes, 2006); however, further research is required to establish its long term environmental fate before it accepted as an agricultural management practice (Dassanayake et al., 2015). The use of chemical amendments to immobilise contaminants can be grouped into aluminium, calcium and iron-based products and are used principally for P sequestration (Udeigwe et al., 2011).

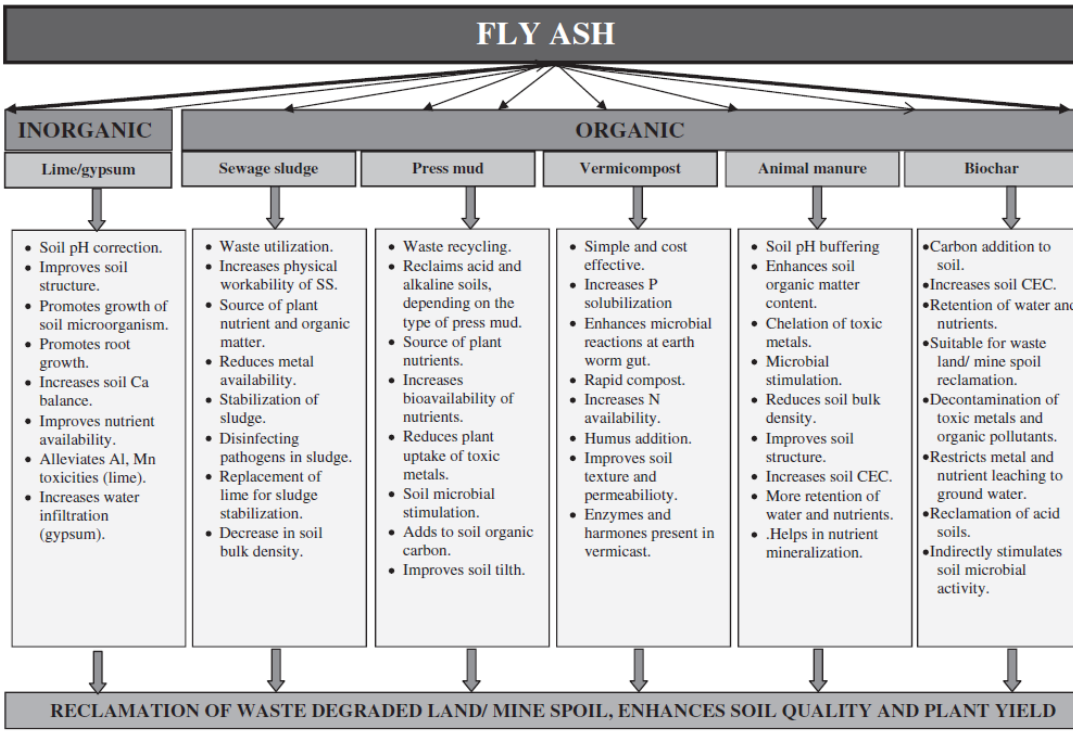

Figure 1.16 Soil amelioration benefits from application of fly ash with various organic and inorganic amendments (Ram and Masto, 2014).

Over the years, several researchers have evaluated the effectiveness of a range of chemical products for immobilizing primary contaminants such as P, N, heavy metals, and organic carbon (Moore and Miller, 1994; Moore et al., 2000; Cox et al., 2005; Udeigwe et al., 2009; Wang et al., 2011; Brennan et al., 2011; Brennan et al., 2014). The choice of chemical amendments largely depends on the availability, contaminant type, and in particular the cost. Chemical amendments have been used as best management practice for poultry litter for over 30 years, driven primarily by the need to improve output by reducing detrimental NH_3 emissions (Moore and Edwards, 2005), but much more research is needed before chemical amendments can be recommended as a best management practice for dairy and pig slurries, and DSW. Impurities such as trace elements, fluoride, and total dissolved salts contained in commonly used industrial wastes such as phosphogypsum and bauxite wastes may be leached to groundwater and/or exported through runoff to receiving water bodies. For example, the use of ochre, when mixed with soil in pellet form, may give structure to the soil, along with the possibility of the mitigation of chronic P losses, but may also give rise to potentially dangerous levels of heavy metals (Fenton et al., 2009).

Zeolites are naturally occurring hydrated crystalline aluminosilicate materials with a porous structure and high cation exchange properties. They have a high capacity to adsorb N, in particular NO_3, and because of their superior hydraulic properties, are suitable for use in filtration-type water treatment processes (Loganathan et al., 2013). Zeolites are also recognised as a remediation technology for heavy metal-contaminated groundwater (Hashim et al., 2011), and natural zeolitic rocks such as clinoptilolite has been shown to remove arsenic from different types of waters (Ruggieri et al., 2008).

Very few studies have examined the potential of zeolites to remove N from agricultural wastewaters (e.g. Nguyen and Tanner, 1998; Meisinger et al., 2001) and as far as the author is aware, no studies have previously assessed the combined effectiveness of zeolite and chemical amendments to mitigate N, P and C losses in surface runoff and leaching losses from land applied agricultural wastes. These studies have since been carried out and are included in Chapters 2, 3 and 4 of this thesis.

1.6 Knowledge gaps and project aims

In order to meet our water quality obligations under the WFD, it is apparent that further investigation of mitigation measures to reduce organic and nutrient losses to surface and ground waters will be necessary. This study aims to address the following knowledge gaps in mitigation of organic and nutrient losses from landspreading of agricultural wastes:

1. There is a need to advance cost effective, low energy and low maintenance on-farm treatment of DSW to reduce the pollution risks arising from repeated landspreading on lands close to farmyards. Additionally, reuse of treated DSW for yard and machinery washing is

increasingly becoming a high priority from the viewpoint of water conservation;

2. There has been little or no research carried out to assess the combined effectiveness of zeolite and chemical amendments to mitigate surface losses of N, P, C and SS from land applied dairy and pig slurries and DSW under repeated rainfall;

3. To the author's knowledge, no research has been carried out to date to examine the effectiveness of mixing zeolite and chemical amendments with dairy and pig slurries and DSW to reduce leaching losses of N, P and C, and GHG emissions of CO_2 and CH_4 under persistent and repeated rainfall.

The hypotheses of this study were that:

1. Combined zeolite and chemical amendments would reduce N, P, C and SS losses in runoff from dairy and pig slurries, and from DSW;

2. Combined zeolite and chemical amendments would reduce leaching losses of N, P and C and gaseous emissions of CO_2 and CH_4 from dairy and pig slurries, and from DSW;

3. Intermittently loaded filters using woodchip media were more effective than those using sand media when treating DSW.

The objectives of this study were:

1. To determine the effects of mixing combined zeolite and chemical amendments with dairy and pig slurries and DSW, on surface losses of N, P, C and SS under different simulated rainfall scenarios following land application to grass soils;

2. To determine the effects of mixing combined zeolite and chemical amendments with dairy and pig slurries and DSW on leaching losses of N, P and C, and GHG emissions of CO_2 and CH_4 following surface application to repacked soils and subjected to repeated simulated rainfall;

3. To determine the impacts of filter depth and organic loading rate (OLR) on the performance of woodchip filters when loaded with DSW and to compare the performance of woodchip and sand filters operated under the same loading conditions.

1.7 Structure of dissertation

This thesis comprises three published papers and one paper currently under review.

Chapter 2 comprises a published paper, "Use of zeolite with alum and PAC amendments to mitigate runoff losses of P, N and suspended solids from agricultural wastes applied to grassed soils" (Journal of Environmental Quality, 2015, 44(5): 1674-1683). This chapter reports on the mitigation of P, N, and SS losses in runoff from grassed soil boxes, onto which dairy slurry, pig slurry, and DSW, were applied with combined amendments of either zeolite and polyaluminum chloride (PAC) with dairy and pig slurries, or zeolite and alum with DSW. This chapter contributes to the first objective of this study.

Chapter 3 comprises a published paper, "Zeolite combined with alum and polyaluminum chloride mixed with agricultural slurries reduces carbon losses in runoff from grassed soil boxes" (Journal of Environmental Quality, 2016, 45(6): 1941-1948). This chapter quantifies (i) total C losses in runoff to surface waters after land application of dairy slurry, pig slurry, and DSW, and (ii) the effectiveness of applying combined amendments of either zeolite and PAC with dairy and pig slurries, or zeolite and alum with DSW, to mitigate these losses. This chapter also contributes to the first objective of this study.

Chapter 4 reports on the findings of a laboratory study to investigate if zeolite and either PAC or alum amendments, applied to dairy and pig slurries and to DSW and surface applied to repacked grassland soil columns, were effective in reducing (i) leached N, P and C losses over a 7-month experimental period, and (ii) CO_2 and CH_4 emissions over a 28-day experimental period. This chapter, "Zeolite, alum and polyaluminum amendments mixed with agricultural slurries to abate nutrients in soil column leachate and greenhouse gas emissions", has been submitted to an international journal for review, and addresses the second objective of this study.

Chapter 5 comprises a published paper, "Assessment of intermittently loaded woodchip and sand filters to treat dairy soiled water" (Water Research, 2016, 103: 408-415). This chapter examines the impacts of filter depth and OLR on the performance of woodchip filters when loaded with DSW and compares them to sand filters operated under the same experimental conditions. An overarching objective of the study was to contribute to an improved understanding of the factors that should be considered in the design, construction and management of passive woodchip filters to treat on-farm DSW. This chapter addresses the third objective of this study.

Chapter 6, the final chapter details the conclusions and recommendations arising from this research.

1.8 Research dissemination

The following is a list of research outputs from this thesis, including peer reviewed journal papers, manuscripts in preparation, and conference presentations.

1.8.1 Peer reviewed journal papers

Murnane, J.G., Brennan, R.B., Fenton, O. and Healy, M.G., 2016. Zeolite Combined with Alum and Polyaluminum Chloride Mixed with Agricultural Slurries Reduces Carbon Losses in Runoff from Grassed Soil Boxes. *J. Environ. Qual. 45(6),* 1941-1948.

Murnane, J.G., Brennan, R.B., Healy, M.G. and Fenton, O., 2016. Assessment of intermittently loaded woodchip and sand filters to treat dairy soiled water. *Water Research, 103*, 408-415.

Murnane, J.G., Brennan, R.B., Healy, M.G. and Fenton, O., 2015. Use of zeolite with alum and polyaluminum chloride amendments to mitigate runoff losses of phosphorus, nitrogen, and suspended solids from agricultural wastes applied to grassed soils. *J. Environ. Qual. 44(5)*, 1674-1683.

1.8.2 Manuscripts in preparation

Murnane, J. G., Fenton, O. and Healy, M.G., 2017. Zeolite, alum and polyaluminum amendments mixed with agricultural slurries to abate nutrients in soil column leachate and greenhouse gas emissions. (Submitted paper, February 2017).

1.8.3 Conference presentations

Murnane, J.G., Lanigan, G., Healy, M.G. and Fenton O. (2016). Amendments for the reduction of nitrogen, phosphorus and carbon in agricultural wastewater surface runoff. Livestock Waste 2016 Conference: Pollution Control and Resource Recovery for the Livestock Sector NUI Galway, 10 – 12 August 2016. (Poster Presentation)

Murnane, J.G., Healy, M.G. and Fenton O. (2016). Comparison of intermittently loaded laboratory filter systems to treat dairy soiled wastewater. 26th Annual Irish Environmental Researchers Colloquium, University Of Limerick 22-24th March 2016. (Oral Presentation)

Murnane, J.G., Healy, M.G. and Fenton O. (2016). Zeolite combined with alum and PAC amendments mitigate carbon losses in runoff from organic agricultural slurries applied to grassed soils. Natural Organic Matter & Trihalomethanes - National Technical Workshop, Hotel Meyrick, Galway, 16 - 17th June 2016. (Poster Presentation)

Murnane, J.G., Healy, M.G. and Fenton O. (2015).Sequestration of phosphorus and nitrogen from agricultural wastewaters using a natural zeolite amendment and subsequent regeneration of the nutrients. Teagasc Agricultural Catchment Programme (ACP) Catchment Science into Policy, Killeshin Hotel, Portlaoise, 13th March 2015. (Poster Presentation)

Murnane, J.G., Healy, M.G. and Fenton O. (2014) Use of zeolite with alum and PAC amendments to mitigate runoff losses of P, N and suspended solids from agricultural wastes applied to grass soils. NUIG/UL Research Day, 21st April 2015, NUIG. (Poster Presentation)

Murnane, J.G., Healy, M.G. and Fenton O. (2014) Dual use of Zeolite and Chemical Amendments to Mitigate Mixed Contaminant Losses in Agricultural Runoff. NUIG/UL Research Day, 20th May 2014, UL. (Poster Presentation)

Murnane, J.G., Healy, M.G. and Fenton O. (2014) Investigation of zeolite and chemical amendments to control phosphorus, nitrogen and suspended solids in runoff from agricultural wastewaters. 24th Annual Irish Environmental Researchers Colloquium, Trinity College Dublin 26 - 28th February 2014. (Oral Presentation)

Murnane, J.G. (2013) Sequestration of phosphorus and nitrogen from agricultural wastewaters and subsequent regeneration of phosphorous. Industry Collaboration, Enterprise Research Centre University of Limerick, 14th May 2013. (Oral Presentations)

Murnane, J.G. (2013) Sequestration of phosphorus and nitrogen from agricultural wastewaters and subsequent regeneration of phosphorous. NUIG/UL Research Day, 11th April 2013, NUIG. (Poster Presentations)

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Chapter 2

The first hypothesis of this thesis was that combined zeolite and chemical amendments would reduce nitrogen (N), phosphorus (P), carbon (C) and suspended solids (SS) losses in runoff from three types of agricultural wastes, dairy and pig slurries, and dairy soiled water (DSW). The study included in this chapter partially addresses this hypothesis and describes a laboratory-based rainfall simulation study designed to measure runoff losses of N, P and SS from grass soils which had been surface applied with the three types of unamended and amended wastes. A further study to measure runoff C losses from the unamended and amended wastes is later described in Chapter 3 and thus the combined findings of chapters 2 and 3 address the first hypothesis of this thesis.

The contents of this chapter have been published in Journal of Environmental Quality *[J. Environ. Qual. 44:1674–1683 (2015)]*. John Murnane designed and set up the experiment, carried out all of the testing and analysis, and is the primary author of this publication. Dr. Mark G. Healy contributed to the experimental design and paper writing. Prof. Owen Fenton and Dr. Ray Brennan assisted with the paper editing and the statistical analysis. The published paper is included in Appendix A.

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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Abstract

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

2.1 Introduction

Excessive application of agricultural waste to soils may have environmental impacts, including phosphorus (P), nitrogen (N) and suspended solids (SS) losses, and increase greenhouse gas emissions (Smith et al., 2001a; Chadwick et al., 2011; Kröger et al., 2013; McDowell and Hamilton, 2013). Loss of P, N and SS in overland flow is affected by the time interval between surface application and rainfall events (Allen and Mallarino, 2008; Hanrahan et al., 2009), antecedent hydrologic conditions (Brennan et al., 2012), flow path length (McDowell and Sharpley, 2002), surface slope (Alaoui et al., 2011), soil type (Wall et al., 2013), and the short and long-term effects of agricultural waste application to the soil structure (McDowell et al., 2004). Event P losses in surface runoff following land application of agricultural wastes may be dominated by particulate phosphorus (PP) (Preedy et al., 2001) or by dissolved phosphorus, depending on individual circumstances such as grazing animals, type of stock, topography and degree of exposure of the soil to rainfall events (Hart et al., 2004), whereas most of the permanent P losses in surface runoff from soils are in dissolved form (Heathwaite and Dils, 2000). Nitrogen losses are dominated by ammonium (NH_4-N) (Heathwaite et al., 1996; Smith et al., 2001a). Suspended sediment is an important carrier of contaminants (Quinton and Catt, 2007) and, depending on the soil type and rainfall characteristics, P enriched soil particles may increase the proportion of PP in surface runoff (McDowell et al., 2001; Miller et al., 2009).

With European policy advocating farm intensification (Department of Agriculture, Food and the Marine, 2013), farmers may have no choice but to spread agricultural waste on land with a high soil P. Land spreading remains the most economical and widespread disposal practice for agricultural wastes (e.g. Nolan et al., 2012). Use of chemical amendments applied to agricultural waste to reduce P losses in surface runoff following land application has been shown to be effective (Smith et al., 2001b; Kalbasi and Karthikeyan, 2004; Moore and Edwards, 2007). In contrast to most studies, Brennan et al. (2012) tested the effect of either poly-aluminum chloride (PAC; $Aln(OH)mCl_3n$-m; 10% Al_2O_3), alum ($Al_2(SO_4)_3{\cdot}nH_2O$; 8% Al_2O_3), or lime ($Ca(OH)_2$) on both P and N losses. They found that the three chemicals did not have a significant effect on N losses following the first rainfall event two days after slurry application to grassed plots.

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

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

2.2 Materials and Methods

2.2.1 Chemical and physical analyses

2.2.1.1 Agricultural wastes

Total phosphorus (TP) was measured using acid persulphate digestion and dissolved reactive phosphorus (DRP) by centrifuging at 17,970 RCF (relative centrifugal force) for 5 min, filtering through 0.45 µm filters and measuring colorimetrically using a nutrient analyzer (Konelab 20, Thermo Clinical Laboratories Systems, Finland). Total nitrogen (TN) was measured using a BioTector TOC TN TP Analyzer (BioTector Analytical Systems Ltd., Cork, Ireland). Ammonium was extracted from fresh waste by shaking 10 g of waste in 200 mL of 0.1M HCL on a peripheral shaker for 30 min at 200 rpm, centrifuging at 17,970 RCF for 5 min and measuring colorimetrically. Waste pH was measured using a pH probe (WTW, Germany) and dry matter (DM) was measured by drying at 105 °C for 24 h. All parameters were tested in accordance with the standard methods (APHA, 2005).

2.2.1.2 Zeolite

The zeolite was sieved to a particle size of 2.36 – 3.35 mm and analyzed for Al_2O_3, BaO, Fe_2O_3, MnO, TiO_2, and SrO using inductively coupled plasma mass spectrometry (ICP-MS), CaO, MgO, K_2O and Na2O using atomic adsorption spectrometry (AAS), P_2O_5 by colorimetry and SiO_2 by method of fusion (Vogel, 1989).

2.2.1.3 Soil

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

2.2.1.4 Rainfall simulator runoff

Runoff samples were tested for pH using a pH probe and for SS using vacuum filtration of at least 50 mL of well-mixed, previously unfiltered, subsamples through Whatman GF/C (pore size 1.2 µm) filter paper (APHA, 2005). Sub-samples were filtered through 0.45 µm filters and measured colorimetrically for DRP, NH_4-N, total oxidized nitrogen (TON) and nitrite-N (NO_2–N) using a nutrient analyzer (Konelab 20, Thermo Clinical Labsystems, Finland). Unfiltered and filtered sub-samples were tested for TP and total dissolved phosphorus (TDP) respectively using acid persulphate digestion, and unfiltered sub-samples tested for TN using a BioTector Analyzer (BioTector Analytical Systems Ltd., Cork, Ireland).

2.2.2 Materials collection and characterization

2.2.2.1 Agricultural wastes

Three types of agricultural wastes were collected from the Teagasc Research Centre, Moorepark, Fermoy, Co. Cork. They were: (1) dairy slurry, from a slatted unit housing dairy cows (2) pig slurry, from an integrated pig unit and (3) DSW from a milking parlor washwater collection sump. Dairy soiled water is defined as dairy wash water from hard standing farmyard areas contaminated with livestock feces, urine or silage effluent, fertilizers and parlor washings, which have a DM content < 1% and a 5-day biochemical oxygen demand (BOD_5) < 2,500 mg L^{-1}. All wastes were homogenized immediately prior to collection by agitating for 30 min using mechanical agitators. The samples were stored in 25 L containers, which were placed in a temperature-controlled room at 11 °C for 12 h prior to the experimental onset. Triplicate samples of each waste were tested for TP, DRP, TN, NH_4-N, pH and DM (Table 2.1).

2.2.2.2 Zeolite

The zeolite used in this study was of Turkish origin and the sieved zeolite (2.36 – 3.35 mm), comprised mainly silica (66.7% SiO_2) and aluminum (10.4% Al_2O_3) (Table 2.2).

2.2.2.3 Soil

Intact grassed soil samples, 500 mm long, 300 mm wide and 100 mm deep, were collected from grassland, which had not received fertilizer application for more than 10 yr, in Galway City, Republic of Ireland. The soil was a poorly drained sandy loam (57±5% sand, 29±4% silt and 14±2% clay) with a Pm of 2.8 ±0.5 mg kg^{-1} (mg P L^{-1}), a WEP of 2.3±0.4 mg P kg^{-1}, a pH of 6.4±0.3 and an organic matter content of 5±2%. The soil type is classified as an acid brown earth Cambisol (WRB classification).

Table 2.1 Waste characterization for total phosphorus (TP), dissolved reactive phosphorus (DRP), total nitrogen (TN), ammonium (NH4-N), pH and dry matter (DM) (*n*=3). The characterizations were carried out over the full experimental period of the study.

Waste Type	TP	DRP	TN	NH_4-N	pH	DM
	------------- mg L^{-1} -------------					%
Dairy slurry	563±55	18±4	4174±554	1800±16	7.78±0.03	8.0±0.1
Pig slurry	619±30	42±1	2648±242	1814±87	7.49±0.05	2.6±0.1
Dairy soiled water	52±11	17.±1	748±76	163.7±3.0	6.89±0.01	0.7±0.3

Table 2.2 Chemical composition of natural zeolite used. The zeolite was sieved to a particle size of 2.36-3.35 mm. All values expressed as percentages.

Al_2O_3	BaO	Fe_2O_3	MnO	SiO_2	CaO	MgO	K_2O	Na2O	TiO_2	P_2O_5	SrO	Loss in ignition at 1000 °C
10.4	0.03	0.90	0.01	66.7	1.57	0.52	4.73	0.86	0.06	<0.001	0.04	14.1

2.2.3 Adsorption capacity of zeolite

The ability of zeolite to remove P (PO_4-P) and N (NH_4-N) from the three types of wastes was first investigated using a multi-point Langmuir isotherm (McBride, 2000):

$$\frac{C_e}{x/m} = \frac{1}{ab} + \frac{C_e}{b} \qquad (1)$$

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

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

2.2.4 Optimum zeolite application

Bench-scale tests were used to establish optimum application ratios of zeolite (expressed as g zeolite per g DM of waste) for NH_4-N removal for each of the wastes. Sieved zeolite (2.36 – 3.35 mm) was added (n=3) in amounts ranging from 1 to 15 g to 40 mL of each waste type in 100 mL containers. All containers were sealed and placed on a reciprocating shaker for 24 h at 250 rpm. The samples were then allowed to settle for 1 h, centrifuged at 17,970 RCF for 5 min and tested for NH_4-N by adding 25 mL of the supernatant to 500 mL of 0.1M HCL, shaking for 30 min at 200 rpm, filtering through 0.45 μm filter paper and measuring colorimetrically. The optimum application ratio was defined as the mass of zeolite above which there was little or no enhanced rate of NH_4-N removal in the supernatant, or where the volume of zeolite comprised no greater than 10% of the volume of waste.

To reduce WEP, the following chemicals were mixed with the wastes to which zeolite had been applied at the established optimum ratios for NH_4-N removal: (1) PAC comprising 10% Al_2O_3 to the dairy slurry at five Al:TP stoichiometric ratios between 0.5:1 and 1.5:1 (2) PAC comprising 10% Al_2O_3 to the pig slurry at five Al:TP stoichiometric ratios between 0.3:1 and 1.25:1; and (3) alum comprising $Al_2(SO_4)_3{\cdot}18H_2O$ to the DSW at five Al:TP stoichiometric ratios between 5:1 and 12:1. The combination of amendments that produced the best reductions of NH_4-N concentrations and WEP from the wastes were used in the runoff experiments.

2.2.5 Rainfall simulation study

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

2.2.5.1 Runoff boxes and rainfall simulation

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

This experiment used laboratory runoff boxes, 1 m long by 0.225 m wide by 0.05 m deep with side walls 25 mm higher than the soil surface and 5 mm diameter drainage holes each located at 0.3 m intervals along the base (Regan et al., 2010). The runoff boxes were positioned at a 10% slope to the horizontal, and all surface runoff was collected at the downstream end using an overflow weir with the crest positioned at the same level as the soil surface. Muslin cloth was placed at the base of each laboratory runoff box to prevent soil loss through the drain holes at the base before packing the soil. Intact grassed cores from the study site were transported to the laboratory and stored at 11 °C prior to testing. All experiments were carried out within 14 d of soil core collection. Immediately prior to the start of each runoff box experiment, each core was trimmed to a typical length of between 450-500 mm and butted against an adjacent core to form a continuous surface of between two and three cores. Molten candle wax was used to seal any gaps between the cores and the sides of the runoff box. The grass on the soil samples was cut to an approximate length of 25 mm to simulate freshly cut meadow conditions.

The drain holes at the base of each runoff box were initially plugged and the soil cores were then saturated using a rotating disc, variable-intensity rainfall simulator (Williams et al., 1998) until ponding occurred on the soil surface. The soil was then left to drain for 24 h to replicate field capacity conditions before the experiment commenced. At t = 24 h, the drain holes were sealed and remained so for the remainder of the experiment. At this point (t = 24 h), unamended wastes and wastes amended with either a combination of zeolite and PAC/alum amendment or PAC/alum amendment only, were spread on the soil and left for 48 h. At t = 72 h, 96 h and 120 h, successive rainfall events (RE1, RE2, RE3), with an intensity of approximately 10 mm h^{-1} (2-yr, 1-h rainfall event), were applied to the same sod in each runoff box. Each event lasted for 30 min after continuous runoff was observed. Surface runoff samples for each event were collected at 5 min intervals over this 30 min period and tested immediately following each rainfall simulation.

2.2.5.2 Runoff analysis

Each of the samples taken at 5 min intervals was tested for pH and for SS. Filtered sub-samples, also taken at 5 min intervals, were measured for TDP, DRP, NH_4-N, TON and NO_2–N. Nitrate-N was calculated by subtracting NO_2–N from TON. Unfiltered sub-samples, taken at 10, 20 and 30 min after continuous runoff were tested for TP and TN. Dissolved unreactive phosphorus (DUP) was calculated by subtracting DRP from TDP and PP was calculated by subtracting TDP from TP.

2.2.5.3 Data analysis

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

2.3 Results

2.3.1 Adsorption Capacity and bench scale studies

The monolayer adsorption capacity of zeolite, q_{max}, ranged from 0.06 (pig slurry) to 0.31 (dairy slurry) mg PO_4-P g^{-1} and from 0.74 (DSW) to 7.88 (pig slurry) mg NH_4-N g^{-1}. The optimum combined amendment application rates for reduction of both PO_4-P and NH_4-N for dairy slurry were 2 g g^{-1} DM of zeolite with a stoichiometric PAC ratio of 1.25:1 (Al:TP). The corresponding rates for pig slurry were 6 g g^{-1} DM of zeolite with a stoichiometric PAC ratio of 1:1 (Al:TP) and for DSW, 10 g g^{-1} DM of zeolite with a stoichiometric alum ratio of 5:1 (Al:TP).

2.3.2 Runoff from laboratory rainfall simulation study

2.3.2.1 Phosphorus

The average FWMCs of TP and DRP in runoff over the three rainfall events increased significantly ($p<0.001$) for all unamended waste applications when compared to the control soil. With the exception of DSW, TP concentrations were reduced ($p<0.001$) following application of PAC and alum amended (without zeolite addition) wastes, and DRP concentrations were reduced for dairy and pig wastes ($p<0.001$) and for DSW ($p<0.01$) (Figure 2.1, Table 2.3). Further reductions in TP were measured for dairy and pig wastes ($p<0.001$) amended with combined zeolite and PAC/alum, however DRP concentrations were not significantly different.

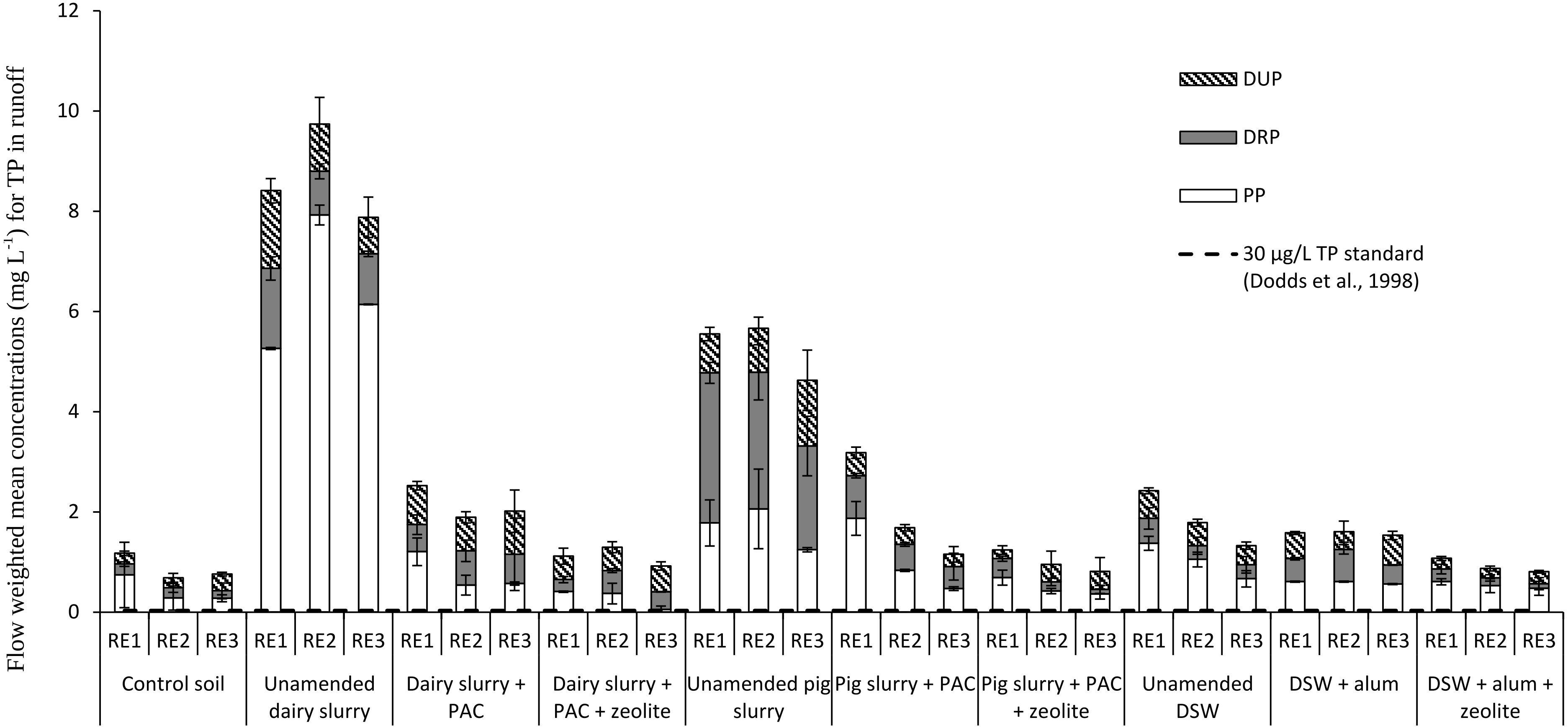

Figure 2.1 Histogram of flow weighted mean concentrations for total P (TP) comprising particulate P (PP), dissolved reactive P (DRP), and dissolved unreactive P (DUP) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h. Data regarding TP standard are from Dodds et al. (1998). DSW, dairy-soiled water; PAC, polyaluminum chloride.

Table 2.3 Flow weighted mean concentrations in runoff averaged over three rainfall events and % reductions (% R) from unamended slurries for total P (TP), particulate P (PP), total dissolved P (TDP), dissolved reactive P (DRP), dissolved unreactive P (DUP), total N (TN), ammonium (NH_4-N), nitrite (NO_2-N), nitrate (NO_3-N), suspended solids (SS) and pH, and % reduction or increase from unamended waste pH in runoff.

Waste application	TP ($mg\ L^{-1}$)	% R	PP ($mg\ L^{-1}$)	% R	TDP ($mg\ L^{-1}$)	% R	DRP ($mg\ L^{-1}$)	% R	DUP ($mg\ L^{-1}$)	% R	TN ($mg\ L^{-1}$)	% R	NH_4-N ($mg\ L^{-1}$)	% R	NO_2-N ($\mu g\ L^{-1}$)	% R	NO_3-N ($\mu g\ L^{-1}$)	% R	SS ($mg\ L^{-1}$)	% R	pH	% reduction (-) / increase (+) from unamended slurry pH in runoff
Control soil	0.87	-	0.43	-	0.44	-	0.19	-	0.25	-	9.64	-	3.37	-	9	-	36	-	27	-	6.43	-
D(U)	8.68	-	6.44	-	2.23	-	1.16	-	1.07	-	41.00	-	16.53	-	380	-	325	-	535	-	6.73	-
D(CA)	2.14	75	0.77	88	1.37	39	0.60	48	0.77	28	25.54	40	7.11	57	179	53	180	45	198	63	6.30	-6.4
D(A)	1.11	87	0.28	96	0.83	63	0.35	70	0.48	55	18.08	56	5.25	68	131	66	167	49	143	73	6.37	-5.4
P(U)	5.28	-	1.69	-	3.59	-	2.60	-	0.99	-	41.02	-	26.10	-	42	-	168	-	101	-	6.58	-
P(CA)	2.00	62	1.06	38	0.95	74	0.60	77	0.35	65	35.56	13	26.65	-	62	-	175	-	52	49	6.67	1.3
P(A)	1.00	81	0.49	71	0.51	86	0.22	92	0.29	70	22.48	45	13.95	47	42	1	115	31	57	44	6.21	-5.6
DSW(U)	1.84	-	1.03	-	0.81	-	0.35	-	0.46	-	25.95	-	12.43	-	11	-	42	-	112	-	6.08	-
DSW(CA)	1.57	15	0.59	43	0.98	-	0.49	-	0.49	-	23.98	8	8.46	32	13	-	31	26	48	57	5.93	-2.5
DSW (A)	0.92	50	0.54	48	0.38	53	0.17	53	0.21	54	14.33	45	3.37	73	14	-	26	38	85	25	6.95	14.3

% R	% Reduction
D(U)	Unamended dairy slurry
D(CA)	Dairy slurry amended with PAC at 1.25:1 Al:TP (704 $mg\ L^{-1}$)
D(A)	Dairy slurry amended with zeolite at 2 $g\ g^{-1}$ DM (160 $kg\ m^{-3}$) and PAC at 1.25:1 Al:TP (704 $mg\ L^{-1}$)
P(U)	Unamended pig slurry
P(CA)	Pig slurry amended with PAC at 1:1 Al:TP (619 $mg\ L^{-1}$)
P(A)	Pig slurry amended with zeolite at 6 $g\ g^{-1}$ DM (156 $kg\ m^{-3}$) and PAC at 1:1 Al:TP (619 $mg\ L^{-1}$)
DSW(U)	Unamended dairy soiled water
DSW(CA)	Dairy soiled water amended with alum at 5:1 Al:TP (260 $mg\ L^{-1}$)
DSW(A)	Dairy soiled water amended with zeolite at 10 g g-1 DM (70 $kg\ m^{-3}$) and alum at 5:1 Al:TP (260 $mg\ L^{-1}$)

2.3.2.2 Nitrogen

The FWMC for TN from the control soil ranged from 8.5 (RE1) to 11 mg L^{-1} (RE3). The TN concentrations in runoff were observed to increase for all unamended slurry applications compared to the control soil ($p<0.001$). Ammonium-N concentrations were highest for pig slurry, followed by dairy slurry and DSW, while TON concentrations in runoff, primarily as NO_3-N, were highest for dairy slurry, followed by pig slurry and DSW (Table 2.3). The FWMC of TN, NH_4-N and NO_3-N in runoff for chemically amended wastes (without zeolite addition) over the three rainfall events were reduced by 40%, 57% and 45% (dairy slurry), 13%, 0% and 0% (pig slurry), and 8%, 32% and 26% (DSW) compared to unamended wastes. Application of combined zeolite and chemical amendments further reduced TN, NH_4-N and NO_3-N concentrations in runoff from all three wastes over the three rainfall events to below those achieved by chemical amendments only (Figure 2.2). Decreases in TN of amended wastes compared to unamended wastes were significant for all treatments, except for alum-amended DSW and PAC amended pig slurry ($p<0.001$). The TN concentrations in runoff using dual zeolite and PAC/alum amendments were less than those using PAC/alum amendments only for all wastes ($p<0.001$). The combined amendments reduced NO_3-N concentrations in runoff below those of unamended wastes by 49% for dairy slurry (325 to 167 μg L^{-1}), 31% for pig slurry (168 to 115 μg L^{-1}), and 38% for DSW (42 to 26 μg L^{-1}).

2.3.2.3 Suspended solids

The average FWMC of SS from the control soil (27 mg L^{-1}) for all three rainfall events increased significantly ($p<0.001$) following application of unamended wastes (Figure 2.3). The average FWMC of SS from wastes amended with PAC and alum reduced by 63% (dairy slurry), 49% (pig slurry) and 57% (DSW) compared to unamended controls. These removals did not change significantly for dairy and pig slurries (73% and 44%) using dual zeolite and chemical amendments, and resulted in higher SS concentrations for DSW amended with dual zeolite and alum (85 mg L^{-1}) than with alum only (48 mg L^{-1}). The average FWMC of PP in runoff was highly correlated with corresponding SS concentrations for dairy slurry ($R^2 = 0.92$) and to a lesser extent for pig slurry ($R^2 = 0.64$) and DSW ($R^2 = 0.50$) (Figure 2.4).

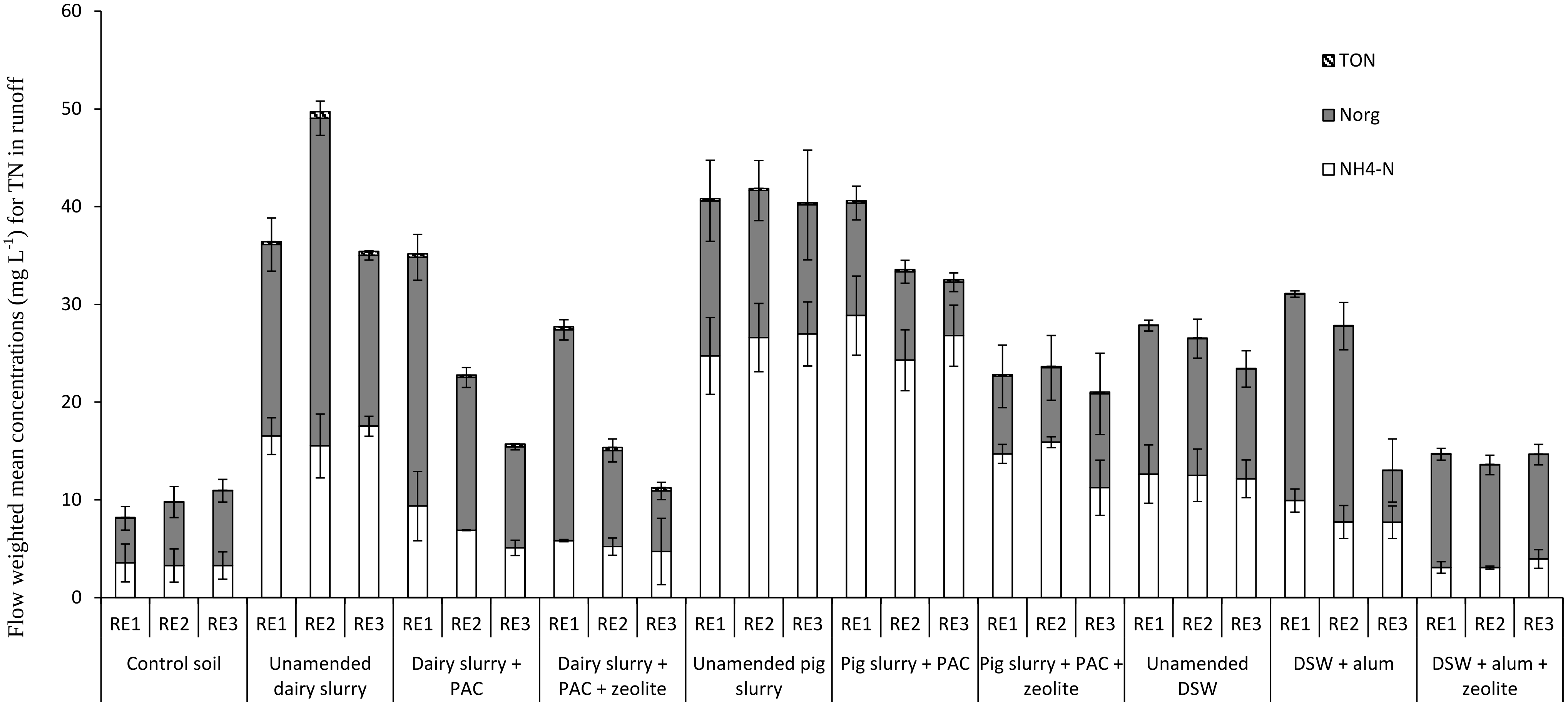

Figure 2.2 Histogram of flow weighted mean concentrations for total N (TN) comprising NH_4-N, organic N (N_{org}) and total oxidized N (TON) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h. DSW, dairy-soiled water; PAC, polyaluminum chloride.

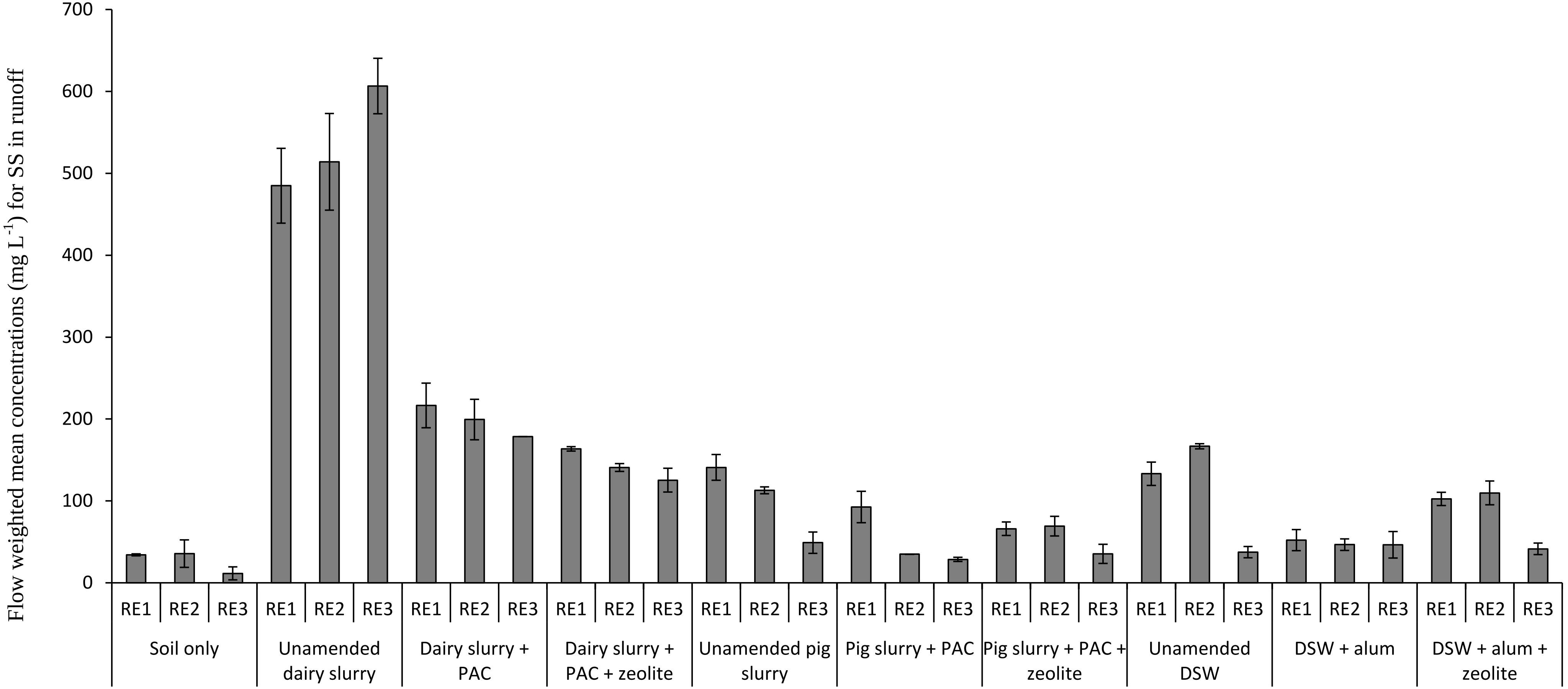

Figure 2.3 Histogram of flow weighted mean concentrations for suspended sediment (SS) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h, and rainfall event 3 (RE3) at t = 120 h. DSW, dairy-soiled water; PAC, polyaluminum chloride.

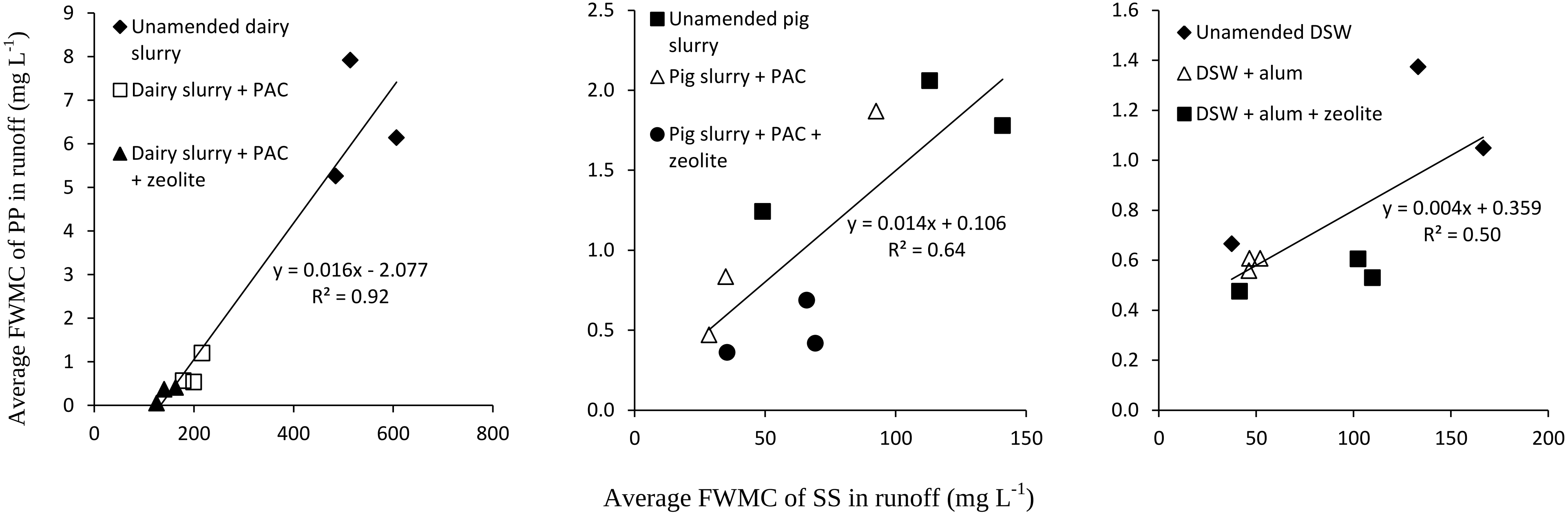

Figure 2.4 Correlation between suspended solids (SS) concentrations and corresponding particulate P (PP) concentrations for dairy slurry, pig slurry and dairy-soiled water (DSW) averaged over all three rainfall events. The data include unamended wastes, wastes amended with polyaluminum chloride (PAC)/alum only (no zeolite), and combined zeolite and PAC/alum amendments. Lines represent a least squares regression analysis, with correlation coefficients (R^2) indicated.

2.3.2.4 pH

Over the three rainfall events, the average pH in runoff from PAC-amended dairy slurry was lower than unamended dairy slurry (Table 2.3). There was no significant difference in pH between unamended and PAC-amended pig slurry and unamended and alum-amended DSW (Table 2.3). The average pH in runoff over the three rainfall events from dairy and pig slurries amended with zeolite and PAC was lower than that for unamended slurries, but was higher in runoff from DSW amended with zeolite and alum.

2.4 Discussion

The amendments used in this study had specific removal capacities, predominantly zeolite for N removal and PAC/alum for P and SS removal. The combinations used were those that produced the best reductions of NH_4-N and WEP from the wastes (Section 2.2.4). The use of packed soil boxes and simulated rainfall is recognized as a practical, if limited, method to assess P transport from grassed and bare soils (Sharpley and Kleinman, 2003; Kleinman et al., 2004).

2.4.1 Phosphorus in runoff

Observed reductions in P using only PAC/alum amendments (without zeolite) were generally consistent with previous studies (Smith et al., 2001b; Elliott et al., 2005; O’Rourke et al., 2012). The average concentrations of TP in runoff following application of unamended dairy slurry increased from 0.87 mg L^{-1} for the control soil to 8.7 mg L^{-1}. This is consistent with the findings of Preedy et al. (2001), who recorded peak TP concentrations of 7 mg L^{-1} from dairy slurry (6% DM) exposed to 28 days of intermittent rainfall ranging in intensity from 0.2 – 3 mm h^{-1} rainfall in a lysimeter plot study. The reduced runoff concentrations in TP and DRP for dairy slurry using PAC at a ratio of 1.25:1 Al:TP (87% and 70%, respectively) were similar to those reported by Hanrahan et al. (2009) (89% and 65%, respectively) at a time interval of 5 d between application of dairy waste and a simulated rainfall event. In the current study, reductions in TP for dairy slurry are dominated by reductions in PP (6.44 to 0.77 mg L^{-1}), and the average FWMC of PP and SS in runoff were related to one another (Figure 2.4). The comparatively high DM content of dairy slurry compared to the other wastes (Table 2.1) meant that, when applied to the soil, much of it remained on the surface for the duration of the experiment. This contrasted with the pig slurry and DSW, which infiltrated the soil quite quickly after application because of their lower DM contents. The position of the dairy slurry on the soil facilitated a higher direct exposure to rainfall compared to the other applied wastes, and resulted in higher runoff SS (Figure 2.3) and PP concentrations (Figure 2.1). Eroded P-enriched particles can be mobilized by rain splash detachment, flow detachment or dispersion (Miller et al., 2009), and may be transported significant distances (Sharpley et al., 1999). Our results indicate that suspended dairy slurry solids, as opposed to soil solids, may be the principal transport mechanism for runoff P, predominantly as PP, from unamended slurry. The addition of PAC and PAC/zeolite to the dairy slurry reduced SS and PP concentrations. It is likely that release of Al^{3+} flocculants from the PAC reduced the extent of fragmentation of the slurry into primary particles, hence reducing the concentration of SS transported by overland flow. The ratio of PP:TP reduced from 0.74 for unamended slurry to 0.36 for PAC amended slurry and 0.25 for combined zeolite and PAC amended dairy slurry, confirming that PAC, and not zeolite, is the most effective of the two amendments in binding PP.

The SS concentrations in runoff from unamended pig slurry were much lower than those of unamended dairy slurry, as were the TP concentrations. The correlation between PP and SS for pig slurry was not as strong as for dairy slurry (Figure 2.4). This was likely due to the lower DM content of the pig slurry (Table 2.1). As a consequence, it is likely that the same opportunity for particle segregation from the slurry was not available and thus PP in runoff was not as prevalent as for dairy slurry (PP:TP = 0.32). The addition of PAC amendment only (no zeolite) increased the PP:TP ratio to 0.53, while the ratio for dual zeolite and PAC was similar (0.49). The overall DRP removal rates for pig slurry were similar to those of previous studies. In a runoff experiment to evaluate the impact of alum and aluminum chloride on swine manure applied to small grassed plots, Smith et al. (2001b) observed DRP reductions of 4.6 mg L^{-1} in runoff between unamended manure and manure treated with 1:1 Al:TP molar ratio. This represented an 84% reduction in DRP, and is comparable to the 77% reduction measured in the current study using PAC at the same ratio. The removal rates in the current study increased to 92% when combined zeolite and PAC amendments were applied.

Very few data exist on runoff P concentrations from DSW applied to grassed soil under simulated rainfall conditions. In a study to measure the effects of rainfall events on P and SS losses from a grassed soil, Serrenho et al. (2012) reported an approximate TP reduction of 80% from relatively dilute DSW (DM = 0.2%, TP = 14.2 mg L^{-1}) amended with alum at a stoichiometric ratio of 8.8:1. They reported a weak correlation ($R^2 = 0.15$) between PP and SS in runoff for the unamended DSW, but a high PP:TP ratio of 0.75. In the current study, a lower stoichiometric ratio (5:1) of alum amendment resulted in a lower TP reduction of 15% for a stronger DSW than that of Serrenho et al. (2012) (Table 2.1). It is likely that application of the higher alum ratio by Serrenho et al. (2012) was more successful in sorbing dissolved P to the soil than in the current study and P-enriched soil particles were then mobilized in runoff. In the current study, both alum and dual zeolite and alum amendments resulted in similar reductions in PP (43% and 48%, respectively) compared to unamended DSW. Use of alum only (no zeolite) did not reduce dissolved P below that of unamended waste. In contrast, dual application of zeolite and alum reduced both DRP and DUP by 53%, indicating that zeolite may have contributed to dissolved P removal in runoff from DSW. The PP:TP ratios for the unamended DSW, alum amended DSW and dual zeolite and alum amended DSW were 0.56, 0.38 and 0.59, respectively. These, combined with the weak correlation between PP and SS in runoff (Figure 2.4), suggest that dissolved P losses may be just as significant as PP losses for the rates of amendments used.

2.4.2 Nitrogen in runoff

The results of this study confirm the results of previous studies using specific amendments in the treatment of agricultural wastes for N (Nguyen and Tanner, 1998; Widiastuti et al., 2011). The observed reductions in runoff NH_4-N concentrations compared to unamended wastes were highest for pig slurry, followed by dairy slurry and DSW (Table 2.3). The reduction in NH_4-N in runoff from dairy slurry amended with PAC (57%) compared to unamended dairy slurry was consistent with the findings of Brennan et al., (2012) (62%). Application of combined zeolite and PAC/alum amendments reduced NH_4-N concentrations in runoff to approximately those of the control soil (3.37 mg L^{-1}) for dairy slurry (5.25 mg L^{-1}) and DSW (3.37 mg L^{-1}), but not for pig slurry (13.95 mg L^{-1}).

The physical composition of the three wastes (Table 2.1) and their appearance on the grassed soil was quite different. While dairy slurry remained on top of the grassed soil, both the pig slurry and DSW infiltrated it more easily. Torbert et al., (2005) observed that the interaction between the applied manure and runoff water is of primary importance for the loss of pollutants. A high interaction between the grass thatch layer and the manure will greatly reduce the amount of manure that leaves the grassed soil as particles, but also increases the interaction that the runoff water has with the surface area of the manure. Although grass was cropped to approx. 25mm in this study, it is likely that the zeolite benefited from more contact time with the dairy slurry than with either the pig slurry or DSW, and this may have resulted in the lower NH_4-N in runoff for the dairy slurry. Conversely, the interaction time between the zeolite and pig slurry may have been insufficient to achieve a similar level of NH_4-N removal as measured for dairy slurry. We are not sure why the NH_4-N runoff removal rate for DSW was so high, but it may be possible that the alum may have sequestered some ammonia, or that pockets of DSW may have pooled on parts of the saturated soil surface, thereby facilitating a higher contact time with the zeolite. The NH_4-N concentrations for both pig and dairy slurries were 1800 mg L^{-1}, while that of the DSW was much lower at 164 mg L^{-1}, and this also may have influenced concentrations of NH_4-N in runoff.

Loss of NH_4-N from land applied wastes is of interest because such losses greatly reduce the fertilizer values of slurry (Misselbrook et al., 2002). More than 50% of applied N can be lost by ammonia volatization, with close to 50% of these emissions occurring in the first 24 h during and after slurry application (Sommer and Hutchings, 2001; Sommer et al., 2003). In an experiment to assess the effects of alum or zeolite addition to dairy slurry on ammonia volatization, Lefourt and Meisinger (2001) found that 65% of ammonia emissions in unamended slurry occurred within 24 h of exposure. Addition of alum at rates of 2.5% and 6.25% reduced these losses by 58% and 57%, respectively, compared to unamended controls, with most of the losses occurring in the initial 12 h and negligible losses thereafter. In the same experiment, addition of zeolite, also at rates of 2.5% and

6.25%, reduced ammonia emissions by 22% and 47%, respectively, compared to the unamended controls, with most of the losses occurring in the initial 24 h period and at a reduced rate thereafter. While the modes of ammonia capture were different for both types of amendments (acidification for alum (Bussink et al., 1994) and availability of NH_4-N exchange sites for zeolite), ammoniacal capture occurred mostly within a 24 h period for both amendments, albeit at a much slower rate for zeolite. In the current study, the zeolite and chemical amendments were added immediately before application of the wastewaters to the flumes and it is likely that some ammonia may have volatilized in the initial 48 h period before the rainfall simulation took place. It may be beneficial, therefore, on a practical basis to add the zeolite to the wastewaters at least 24 h and chemicals at least 12 h prior to landspreading to facilitate reduced ammonia volatilization.

2.4.3 SS in runoff

Suspended sediment in runoff from the control soil was 0.99 kg ha^{-1} and the largest increases following application of unamended wastes were for dairy slurry (19.5 kg ha^{-1}) followed by DSW (4.7 kg ha^{-1}) and pig slurry (4.0 kg ha^{-1}). The large increase for dairy slurry is consistent with its relatively high DM content compared to the other wastes (Table 2.1) and all SS fluxes were likely to have been influenced by the wet antecedent soil conditions. Reductions in runoff SS were highest when all three wastes were amended with PAC/alum only (no zeolite) (Table 2.3). These removal rates did not change significantly for both dairy and pig slurries when amended with dual zeolite and PAC, but reduced for DSW when amended with dual zeolite and alum. This suggests that SS reduction is predominantly due to release of flocculants from the PAC/alum which aids adhesion of the SS in the wastes and in the soil thereby decreasing their susceptibility to loss in runoff. We are not sure why there was an increase in SS concentrations for the DSW when amended with dual zeolite and alum and it is interesting to note that there was no corresponding increase in PP or any of the other P fractions (Table 2.3). One possible explanation for this is that the increased SS might have been mainly in the form of sand (the soil comprised 57% sand) released from the soil surface due to the reduced cover from the DSW compared with the other applied wastes, and which likely had lower P adsorption capacity than either the silt or clay fractions (Hansen et al., 2002).

2.4.4 Cost analysis of amendments

A preliminary cost analysis on use of dual zeolite and PAC/alum amendments indicates that high costs, particularly the cost of zeolite, may be a prohibitive factor in their widespread application. Taking the cost of amendments only (without ancillary costs of storage, application, mixing and spreading) at €1,150 tonne^{-1} for zeolite (in Ireland), €480 tonne^{-1} for PAC and €250 tonne^{-1} for alum, the costs per m^3 of applied slurry based on application rates used in this study is €190 for dairy slurry, €188 for pig slurry and €84 for DSW. These compare with estimated costs per m^3 of €6.40 for dairy slurry, €5.60 for pig slurry and €0.80 for DSW using PAC/alum amendments only (Brennan et al., 2011). Therefore, the additional cost of using dual zeolite and chemical amendments is significantly higher than use of chemical only (by an order of magnitude in excess of 2 in the case of DSW) and consequently may not be an attractive mitigation option in areas where zeolite is not an indigenous natural material and where purchase costs may be prohibitive. Acknowledging that final costs may vary with location and availability of zeolite, it is nevertheless unlikely that widespread use of dual zeolite and chemical amendments in agricultural wastewaters will be economically sustainable in the short to medium term, and would be better suited to critical source areas (areas where there is a high risk of incidental losses in overland flow), or where land availability for spreading agricultural wastes is limited.

2.5 Conclusions

Concentrations of TP and TN in runoff from all wastes amended with dual zeolite and PAC/alum were less ($p<0.001$) than those using only PAC/alum amendments, but there was no significant difference between them for DRP and SS removals. Use of combined zeolite and PAC/alum amendments to reduce P, N and SS in runoff was most effective for dairy slurry followed by pig slurry and least effective for DSW. As expected, PAC/alum had the greatest impact on P and SS removals for all wastes, while zeolite had the greatest impact on N removal. Use of dual amendments at the applied rates did not adversely impact their individual P, N and SS removal capacities, and their application may be most beneficial in targeted areas where there is high risk of incidental mixed contaminant losses in overland flow. Their widespread use, however, may be prohibited by significant associated costs, particularly in regions where zeolite is not an indigenous natural material and purchase costs may be high.

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Chapter 3

The outcomes of a laboratory-based rainfall simulation study to measure runoff losses of nitrogen (N), phosphorus (P) and suspended solids (SS) from unamended and amended dairy and pig slurries and dairy soiled water (DSW) were reported in Chapter 2. In this chapter, the outcomes of a similar study to measure carbon (C) losses from the three types of unamended and amended wastes are described. The combined outcomes of chapters 2 and 3 address the first hypothesis of this thesis, which is that combined zeolite and chemical amendments would reduce N, P, C and SS losses in runoff from dairy and pig slurries, and DSW

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Zeolite combined with Alum and Polyaluminum Chloride mixed with agricultural slurries reduces carbon losses in runoff from grassed soil boxes

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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.

3.1 Introduction

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), North America, and Canada (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 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 $>100\ \mu g\ L^{-1}$ (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.

3.2 Materials and Methods

3.2.1 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).

3.2.2 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 3.1) 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).

Table 3.1 Slurry characterization for total organic C (TOC), total inorganic C (TIC), total P (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.

3.2.3 Slurry Amendments

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

3.2.4 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) 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).

3.2.5 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.

3.3 Results and Discussion

3.3.1 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. 3.1). This was most likely due to the reduced opportunity for alum to flocculate 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. 3.1).

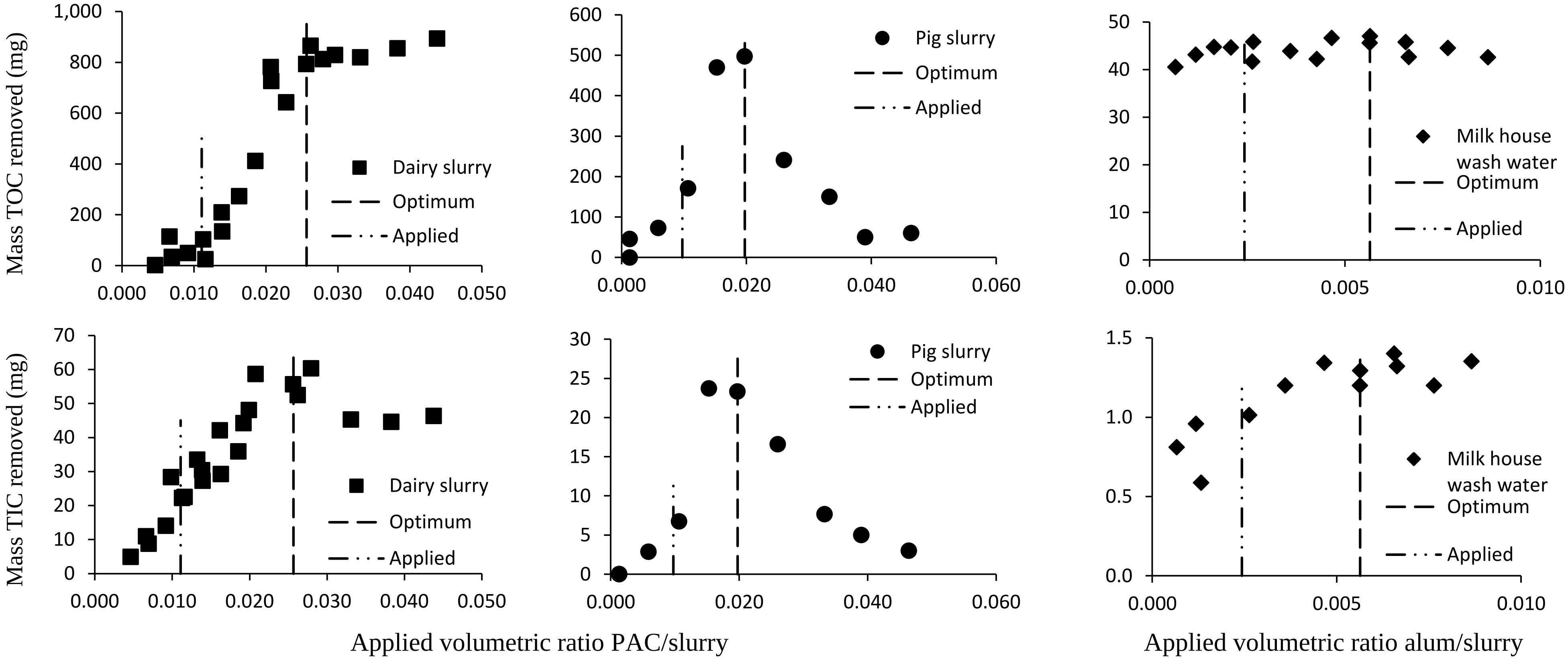

Figure 3.1 Total organic C (TOC) and total inorganic C (TIC) removals in batch study tests (*n* = 3) after application of polyaluminum chloride (PAC) to dairy and pig slurries and alum to milk house wash water (MWW). Optimum volumetric ratios for TOC and TIC removals were 0.0256 and 0.0197 PAC/slurry 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.

The maximum zeolite adsorption capacities for TOC and TIC (Table 3.2) indicate that the ability of zeolite to remove TOC might be affected by the DM of the slurries (Table 3.1), 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.

Table 3.2 Maximum removal rates of total organic C (TOC) and total inorganic C (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.

	Maximum zeolite removal rates				**Maximum PAC / alum removal rates**		
Slurry type	**(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

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 3.2). The reduction of TOC and TIC from the slurries amended with either PAC or alum was via the process of flocculation 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. 3.1) 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).

3.3.2 Rainfall Simulation Study

Significant ($p<0.001$) increases in FWMCs of TOC were observed for all unamended slurry applications over the three rainfall events when compared with the control soil and were highest for dairy slurry followed by pig slurry and MWW (Fig. 3.2). 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. 3.2; Table 3.3). 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 3.3).

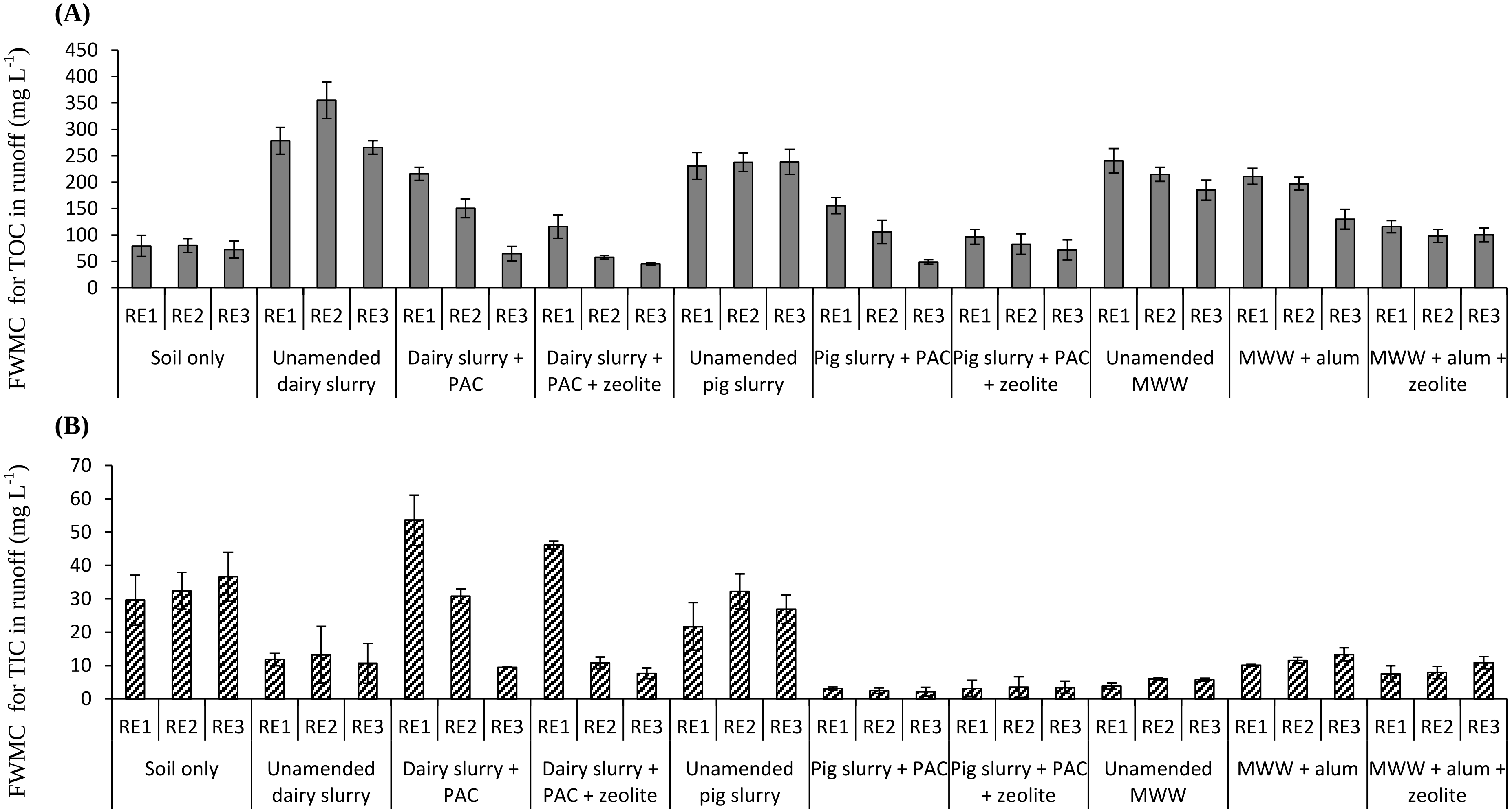

Figure 3.2 Histogram of flow weighted mean concentrations (FWMC) (*n*=3) for (A) total organic C (TOC) and (B) total inorganic C (TIC) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h and rainfall event 3 (RE3) at t = 120 h. Error bars indicate standard deviation.

Table 3.3 Flow weighted mean concentrations in runoff (*n* = 3) averaged over three rainfall events and % reductions (+) or increases (-) from unamended slurries for total organic C (TOC) and total inorganic C (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.

3.3.3 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. 3.3) for both unamended and amended dairy and pig slurries (R^2 = 0.78 and 0.48, respectively) but was not correlated with MWW (Fig. 3.3). 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. 3.3). 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 concentration in eroded sediment to that of the original sediment) 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. 3.1) 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 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 3.3; Fig. 3.2). 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 3.2).

3.3.4 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 3.3) under simulated rainfall even though the PAC/alum was not applied at optimum TOC removal rates (Fig. 3.1). 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 3.4). 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.

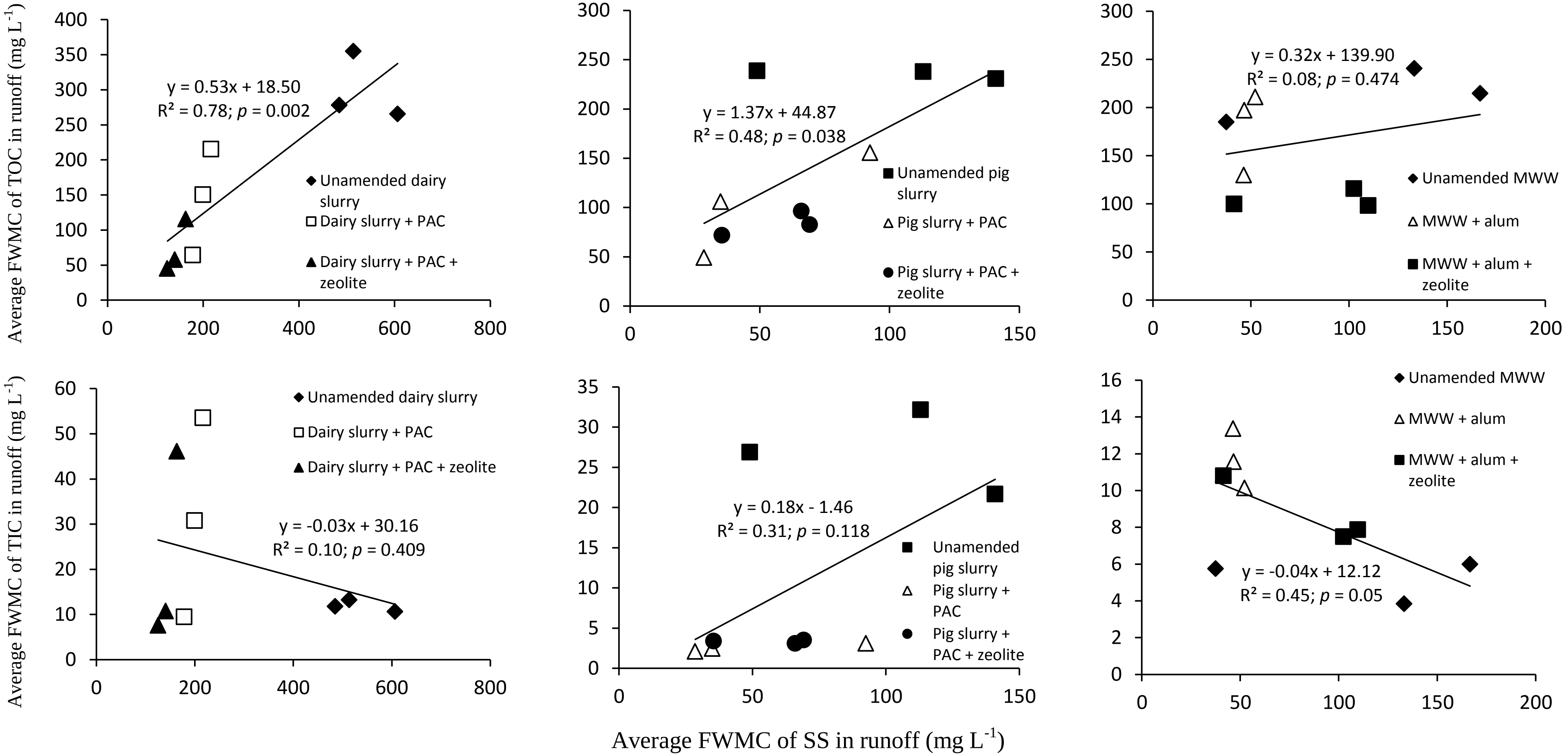

Figure 3.3 Correlation between suspended solids (SS) concentrations and corresponding total organic C (TOC) and total inorganic C (TIC) concentrations ($n = 3$) for dairy slurry, pig slurry and milk house wash water (MWW) averaged over all three rainfall events. The data includes unamended wastes, wastes amended with polyaluminum 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.

Table 3.4 Mass balance of total organic C (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 3.3.

					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….		
Slurry type	Vol. slurry applied	Slurry TOC conc.	Mass TOC applied	Vol. runoff	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

3.4 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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Chapter 4

In chapters 2 and 3, the outcomes of laboratory-based rainfall simulation studies to measure surface losses of nitrogen (N), phosphorus (P), carbon (C) and suspended solids (SS) from unamended and amended dairy and pig slurries and DSW applied to grass soils were described. This chapter describes a follow-on study from these initial two studies and reports on leaching losses of N, P and C from the amended and unamended wastes and gaseous emissions of carbon dioxide (CO_2) and methane (CH_4) in a laboratory-based soil column experiment. The second hypothesis of this thesis, which asserts that combined zeolite and chemical amendments would reduce leaching losses of N, P and C and gaseous emissions of CO_2 and CH_4 from dairy and pig slurries, and from DSW is addressed in this chapter.

The contents of this chapter were submitted to an international journal in February 2017. John Murnane developed the experimental design, set up the experiment, carried out all of the testing and analysis, including the statistical analysis, and is the primary author of this publication. Dr. Mark G. Healy contributed to the experimental design and paper editing. Prof. Owen Fenton assisted with the paper editing.

Zeolite, Alum and Polyaluminum amendments mixed with agricultural slurries to abate nutrients in soil column leachate and greenhouse gas emissions

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Abstract

This study aimed to quantify leaching losses of nitrogen (N), phosphorus (P) and carbon (C), as well as carbon dioxide (CO_2) and methane (CH_4) emissions from stored slurry and from packed soil columns, the surfaces of which were applied with unamended and chemically amended dairy and pig slurries and dairy soiled water (DSW). The amendments to the wastewaters, which were applied individually and together, were: polyaluminum chloride (PAC) and zeolite for pig and dairy slurry, and liquid aluminium sulphate (alum) and zeolite for DSW. The columns were irrigated twice weekly and the leachate collected weekly for nineteen weeks after slurry application. Application of pig slurry resulted in the highest total N (TN) and nitrate-N (NO_3-N) fluxes (22 and 12 kg ha^{-1}), whereas corresponding fluxes from dairy slurries and DSW were not significantly ($p<0.05$) higher than those from the control soil. There were no significant ($p<0.05$) differences in leachate N losses between unamended and amended dairy slurries, unamended and amended pig slurries, and unamended and amended DSW. There were no leachate P losses measured over the experimental duration. Total cumulative organic and inorganic C losses in leachate were highest for unamended dairy slurry (82 and 142 kg ha^{-1}), and these were significantly ($p<0.05$) reduced when amended with PAC (38 and 104 kg ha^{-1}) and with PAC and zeolite (43 and 119 kg ha^{-1}). The highest average cumulative CO_2 emissions for all treatments were measured for pig slurries (680 kg CO_2-C ha^{-1}) followed by DSW (515 kg CO_2-C ha^{-1}) and dairy slurries (486 kg CO_2-C ha^{-1}). The results indicate that pig slurry, either in raw or chemically amended form, poses the greatest environmental threat of leaching losses and gaseous emissions of CO_2 and CH_4 and, in general, amendment of wastewater with PAC, alum or zeolite, does not mitigate the risk of leaching losses and gaseous emissions.

4.1 Introduction

Long term land application of organic fertilizers may result in excessive amounts of nutrients in soil, and may increase the risk of surface and groundwater contamination (Granger et al., 2011). For example, high nitrate (NO_3) concentrations in groundwater above those recommended by the World Health Organization (10 mg NO_3-N L^{-1}) may lead to environmental (Fenton et al., 2009) as well as human health issues associated with methemoglobinemia in infants (WHO, 2004) if used as a drinking water source. Organically derived nitrogen (N), from sources such as manure application, has been shown to be a major contributor to groundwater NO_3 concentrations (Baily et al., 2011), while phosphorus (P) leaching to groundwater is associated with eutrophication of associated surface waters (e.g. Kleinman et al., 2009). Leaching of pathogenic and harmful slurry-borne contaminants such as animal husbandry-derived antimicrobials and hormones, are also of concern to the environment and human health (Lee et al., 2007). This is exacerbated by recent increases in concentrated animal feeding operations, which have led to large volumes of slurries being generated in relatively small areas and spread at rates that exceed plant nutrient demand (Lee et al., 2007).

Landspreading is the most common method of slurry application (Lloyd et al., 2012) and while methods such as sliding shoe and injection are used to limit N losses through ammonia (NH_3) volatization (Sistani et al., 2010), Kayser et al. (2015) concluded that the amount of N input, rather than the method of application, impacts the extent of NO_3-N leaching in organic sandy soils. Migration of water-borne contaminants through soil is a complex physical and chemical process influenced by factors such as (i) flow characteristics, which depend on the soil structure and grain size (ii) filtration effects due to soil micropores, and clogging from applied manure (iii) straining within the organic portion of the applied manure, and (iv) retention of microbes on soil and organic particles by adsorption and adhesion (Unc and Goss, 2004).

Agriculture contributes globally 10-12% of anthropogenic greenhouse gas (GHG) emissions (IPCC, 2007) and land applied organic manures contribute substantially to this (e.g. Rodhe et al., 2015) through the release of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) from carbon (C) and N compounds in the manures and also, indirectly, by affecting soil properties which can increase GHG emissions from soils (Thangarajan et al., 2013). For example, Huang et al. (2004) reported that manures with high C:N ratios may reduce CO_2 emissions and increase soil organic carbon, while manures with low C:N ratios may lead to an increase in soil CO_2 emissions. Emissions of CH_4, which is generated under anaerobic conditions, tend to be limited from slurries which are applied to well aerated soils; however, slurry storage emissions can be substantial and can exceed those from landspreading (Rodhe et al., 2015). Currently in many countries, abatement of such emissions during storage is seen as a cost effective measure to meet national emission targets.

The use of disturbed soil columns to measure leaching and transport of contaminants through soils is a well-established laboratory method (e.g. Guo et al., 2014) and while macropore structure of intact soils is disturbed during the repacking process (Amin et al., 2016), soil columns nevertheless facilitate the investigation of contaminant transport in a homogenous soil under controlled conditions (Murphy, 2007). Previous studies have examined the potential of slurry amendments to mitigate leachate losses and GHG emissions from land applied pig and dairy slurries (O’ Flynn et al., 2013; Brennan et al., 2015), but currently there are no data available to evaluate and compare the effectiveness of zeolite used in combination with chemical amendments to mitigate leaching losses of N, P and C, and emissions of CO_2 and CH_4 (in storage and upon application to land) when applied to dairy and pig slurries and dairy soiled water (DSW). Therefore, the objective of this laboratory-based study was to investigate if zeolite and either poly-aluminium chloride (PAC) or alum amendments, applied to dairy and pig slurries, and to DSW were also effective in reducing (1) leached N, P and C losses over a 7 month experimental period and (2) CO_2 and CH_4 emissions over a 28 day experimental period. The agricultural wastes were surface applied to repacked grassland soil columns and the amendment rates were those used to mitigate N, P and suspended solids (SS) losses from grassed soil in rainfall simulation studies (Murnane et al., 2015).

4.2 Materials and Methods

4.2.1 Soil

Soil samples were taken from the top 0.2 m of a 0.863 ha grass (perennial ryegrass, tyrella diploid [*Lolium perenne* L.]) plot at the Teagasc Agricultural Research Centre, Moorepark, Fermoy, Co. Cork, Ireland and immediately transported to the laboratory. The plot had been grazed by dairy cows and received *c.* 200 to 250 kg N ha^{-1} annually, but no P application, for > 5 yr prior to soil sampling. The soil, which had a loam texture, was air dried, ground to pass a 2 mm sieve and mixed thoroughly to provide homogenous sub-samples at the laboratory. The particle size distribution was determined by hydrometer analysis (ASTM F1632) and organic matter content by weight loss-on-ignition (Sims and Wolf, 1995). Soil total carbon (TC) and total nitrogen (TN) were determined by high temperature combustion (McGeehan and Naylor, 1998) and pH using a soil to distilled water ratio of 2:1. Soil samples were extracted with Mehlich III solution (Mehlich, 1984) and extract P, potassium (K), calcium (Ca), magnesium (Mg) and aluminium (Al) were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Cation exchange capacity (CEC) was determined from Mehlich III analyses by the sum of cations (Ross, 1995). Water soluble organic C (WSOC) was determined by shaking 5 g of dried soil with 50 mL of distilled water for 30 min (*n*=3) and measuring the total organic C (TOC) of the filtered (0.45 μm) supernatant (BS EN 1484) (BSI, 1997) using a BioTector analyzer (BioTector Analytical Systems Ltd). Soil water extractable phosphorus (WEP) was determined by shaking 5 g of dried soil with 25 mL of distilled water for 30 min (*n*=3) and testing the filtered (0.45 μm) supernatant colorimetrically using a nutrient analyser (Konelab 20, Thermo Clinical Laboratories Systems, Finland).

The ability of the soil to adsorb P (measured as dissolved reactive phosphorus, DRP) was investigated in batch experiments by adding 90 mL of varying concentrations (2 – 175 mg P L^{-1}) of synthetic P-spiked water to flasks containing 5 g soil (*n*=3). All samples were shaken on a reciprocating shaker for 24 h at 250 excursions per minute (epm) and on removal, were allowed to settle for 1 h, filtered through a 0.45 μm filter, and tested colorimetrically using a nutrient analyser (Konelab 20, Thermo

Clinical Labsystems, Finland). The data were then modelled using a Langmuir isotherm to establish the maximum soil P-adsorption capacity.

4.2.2 Agricultural slurries

Three types of agricultural wastes (dairy slurry, pig slurry and DSW) were collected in 25 L containers from the Teagasc Agricultural Research Centre, Moorepark, Fermoy, Co. Cork. All slurries were homogenized by mechanical agitation immediately prior to collection and transferred directly to a temperature-controlled room (10.9±0.7 °C) in the laboratory. All slurry samples were tested within 24 h of collection (*n*=3) for TOC and total inorganic carbon (TIC) (BS EN 1484, 1997) and for TN by combustion oxidation followed by spectrophotometry using a BioTector analyzer. Total phosphorus (TP) was measured using acid persulfate digestion and dry matter (DM) was measured by drying at 105 °C for 24 h. Dissolved reactive P was measured colorimetrically using filtered (0.45 µm) subsamples. Ammonium (NH_4-N) was extracted by shaking 10 g of fresh waste in 200 mL of 0.1M HCL on a peripheral shaker for 30 min at 200 rpm, centrifuging at 17,970 RCF for 5 min and measuring colorimetrically. All parameters were tested in accordance with the standard methods (APHA, 2005).

4.2.3 Slurry amendments

The results of a laboratory runoff study by Murnane et al. (2015) determined the optimum combined chemical and zeolite application rates for reductions in NH_4-N and DRP, and these were used in the current study. The applied chemical and zeolite amendments were based on TP concentrations and DM content of the slurries, respectively. The chemical amendments applied were (1) commercial grade liquid PAC (10% Al_2O_3) added to the dairy and pig slurries at rates equivalent to 12.8 and 3.8 kg t^{-1} (0.42 and 0.15 mg per column), and commercial grade liquid aluminum sulphate (alum) (8% Al_2O_3) added to the DSW at a rate equivalent to 1.0 kg t^{-1} (0.04 mg per column). Turkish zeolite (clinoptilolite), comprising 66.7% SiO_2 and 10.4% Al_2O_3, was sieved to 2.36 – 3.35 mm and added at rates equivalent to 202, 133, and 28 kg t^{-1} (6.7, 5.2 and 1.2 g per column) to the dairy and pig slurries and DSW, respectively. All amendments were added to the slurries in 100 mL containers, mixed thoroughly for approximately 1 min before applying immediately by hand to the soil surface.

4.2.4 Column setup

Thirty uPVC columns, each with internal diameter of 0.1 m and depth of 0.3 m, were placed on a timber support frame and located in a temperature-controlled room for 7 months at 10.5±0.5 °C and relative humidity of 89.5±4.0 % (representative of the average temperature and humidity in Ireland). In order to ensure free draining soil conditions, each column was fitted with a perforated end cap at the base above which a 0.05 m layer of 5-10 mm graded gravel was placed to prevent washout of the soil. The columns were then filled in 0.05 m layers to a compacted (ρ_{bulk} = 1.06 g cm^{-3}) depth of 0.2 m with sieved soil (<2 mm), which had been pre-mixed with distilled water to a moisture content (mc) of approximately 33%, matching *in situ* field conditions at the time of collection (April 2016). This mc is typical of the field capacity of a sandy clay loam (Hignett and Evett, 2008). At each layer, soil was pressed against the column wall to avoid preferential flow through the column and the surface of each layer was lightly scarified after compaction and before addition of the next layer to ensure hydraulic connectivity between layers (Plummer et al., 2004).

Each column was irrigated with 160 mL of distilled water (simulating rainfall), applied twice weekly in two 80 mL increments over a 2 h period (representative of a 6-month, 2-h rainfall event) and was equivalent to an annual average rainfall of 980 mm. Drainage water leachate was collected weekly in containers at the base of the columns (Fig. 4.1). Following an acclimatization period (9 wk) to achieve steady-state soil conditions, unamended and amended slurries were surface applied to the columns on week 10. The treatments (n=3) examined were (1) soil only (no slurry) (2) unamended dairy and pig slurries and DSW (3) PAC-amended dairy and pig slurries, and alum-amended DSW, and (4) PAC and zeolite-amended dairy and pig slurries, and alum and zeolite-amended DSW. The slurry applications rates, net of amendments, were equivalent to 39, 46 and 50 t ha^{-1} (33, 39 and 42 g per column) for dairy and pig slurries and DSW. These rates were the maximum permissible

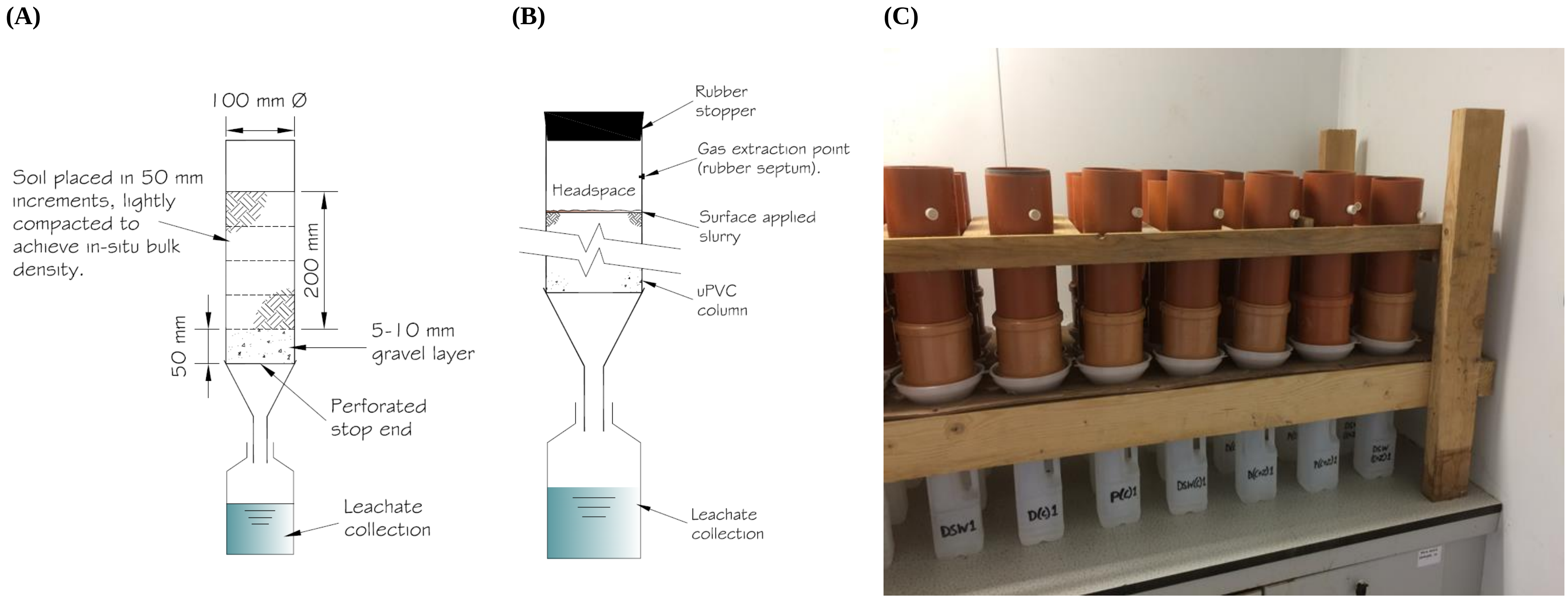

Figure 4.1 Schematic diagrams of typical column setup for leachate sampling (A) and column setup during gas sampling (B) (Not to scale). Image of laboratory set up during the experiment (C).

based on limits of 21 kg P ha^{-1} for dairy slurry, 170 kg N ha^{-1} for pig slurry, and a volumetric limit of 50 m^3 ha^{-1} for DSW (SI No. 31, 2014). Irrigation of the columns with distilled water and leachate collection after slurry application continued at the same rate for the full duration of the experiment.

4.2.5 Leachate analysis

Composite leachate sub-samples were filtered through 0.45 µm filters and measured for (1) DRP, NH_4-N, total oxidized N (TON) and nitrite-N (NO_2–N) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland) (2) total dissolved N (TN_d) and dissolved organic and inorganic C (DOC and DIC) using a BioTector analyzer (BioTector Analytical Systems Ltd.), and (3) total dissolved P (TDP) using acid persulphate digestion. Unfiltered sub-samples were tested for (1) TN, TOC and TIC using a BioTector analyzer (2) TP using acid persulphate digestion, and (3) pH (WTW pH probe, Weilheim, Germany). Calculated parameters were (1) nitrate-N by subtracting NO_2–N from TON (2) particulate N (PN) by subtracting TN_d from TN (3) organic N (N_{org}) by subtracting TON + NH_4-N from TN (4) dissolved organic N (DON) by subtracting TON + NH_4-N from TN_d (5) dissolved unreactive P (DUP) by subtracting DRP from TDP, and (6) particulate P (PP) by subtracting TDP from TP.

4.2.6 Gas sampling and analysis

Gas samples were collected from each column in accordance with Parkin and Venterea (2010) on day 1 (day of slurry applications) and subsequently on days 2, 3, 4, 5, 6, 7, 8, 12, 14, 18, 22 and 28. Raw untreated samples (n=3) of dairy and pig slurries and DSW were also stored in separate columns, from which gas samples were collected on days 1, 2, 3, 7, 9, 13, 17, 24, 31, 38 and 52. A static headspace (0.1 m deep) was formed by sealing the top of each column with a rubber stopper (t = 0 min) and gas samples (7 mL) were withdrawn at 0, 5, 10 and 20 min via a rubber septum placed at the side of the column half way down the headspace (Fig. 4.1). Each sample was injected into a pre-evacuated 6-mL screw cap septum vial and the rubber stoppers were removed after gas collection. On days when gas collection coincided with irrigation of the columns (days 5, 8 and 12), samples were taken 1 h after water application.

All samples were measured for CO_2 and CH_4 using gas chromatography (Agilent Technologies Inc., California, USA). The data were analysed by calculating the rate of change of CO_2 and CH_4 concentrations in the chamber headspace using linear regression. Fluxes (g m^{-2} h^{-1}) were calculated (Troy et al., 2013) as:

$$\text{Flux} = \frac{\Delta\text{Gas x } V_{\text{headspace}} \text{ x } \rho_{\text{gas}}}{100 \text{ x } \Delta t \text{ x } A_{\text{column}}} \qquad (1)$$

where: ΔGas / Δt = rate of change of gas concentration (% h^{-1}); $V_{\text{headspace}}$ = headspace volume (m^3); ρ_{gas} = gas density at operating temperature (g m^{-3}), and A_{column} = column surface area (m^2). Negative fluxes indicated gas uptake within the column, while positive fluxes indicated gas emissions. Cumulative fluxes were determined by multiplying each gas flux by the time interval between sampling.

4.2.7 Measurement of overall environmental impact of treatments

To identify the treatments that had the potential to cause the most environmental damage in terms of GHG emissions and leaching of nutrients and carbon, the cumulative TN and TC losses (kg ha^{-1}) and the cumulative CO_2 and CH_4 losses (expressed as total equivalent CO_2 emissions in kg CO_2-C ha^{-1}) over the study duration were added together (after Healy et al., 2014). Although this method does not take into account legislative drivers which may emphasise potential groundwater impact over gaseous emissions in some countries, it serves to contextualise the study results and allows overall impact of each treatment to be estimated and compared to one another.

4.2.8 Data analysis

Prior to analysis all data were tested for normality and homogeneity of variance to ensure compliance with Gaussian distribution requirements. Differences in leachate flux and gas emissions were assessed using one-way ANOVA in SPSS (IBM SPSS Statistics 20 Core System). Statistical results were considered significant at $\alpha = 0.05$ and all differences discussed in the text are at this significance level.

4.3 Results and Discussion

4.3.1 Soil and slurry classification

The physical and chemical characteristics of the soil are shown in Table 4.1. The soil was classified as a well graded loam, and had a maximum soil P adsorption capacity of 518 mg P kg^{-1} soil (Fig. 4.2). The characterizations of the three agricultural wastes used in this study are shown in Table 4.2.

Table 4.1 Characteristics of the soil used in this study (*n*=3)

Parameter	Value	Units
bulk density	1.06±0.13	g cm^{-3}
% sand	46.9±2.1	%
% silt	36.5±1.2	%
% clay	16.1±0.8	%
D_{10}	0.05±0.00	mm
D_{60}	0.10±0.01	mm
Coefficient of uniformity	1.95±0.22	
Organic matter content	5.19±0.28	%
Total C	2.38±0.01	%
Total N	0.28±0.01	%
C:N	8.65±0.25	
pH	5.99±0.20	
Soil extractable P	88.5±7.8	mg kg^{-1}
Soil extractable K	10.6±11.3	mg kg^{-1}
Soil extractable Ca	1,392±105	mg kg^{-1}
Soil extractable Mg	118.5±7.8	mg kg^{-1}
Soil extractable Al	631±77	mg kg^{-1}
Cation exchange capacity	10.90±0.82	cmol kg^{-1}
Water soluble organic C	58.5±11.4	mg kg^{-1}
Soil water extractable P	1.10±0.49	mg kg^{-1}

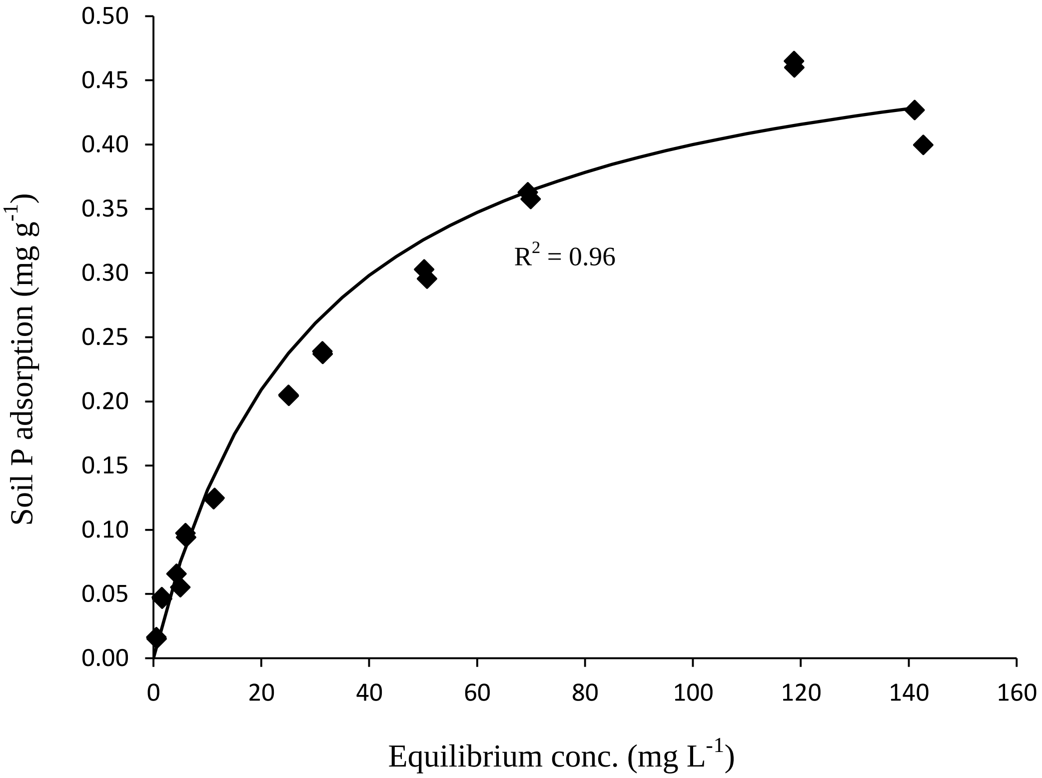

Figure 4.2 Soil P Langmuir adsorption isotherm fitted to measured data (*n*=3). The established maximum adsorption rate (q_{max}) was 518 mg P kg^{-1} soil.

Table 4.2 Slurry characterizations (mean ± standard deviation) (*n*=3) for total N (TN), ammonium (NH_4-N), total P (TP), dissolved reactive P (DRP), total organic C (TOC), total inorganic C (TIC), pH and dry matter (DM).

Slurry type	TN	NH_4-N	TP	DRP	TOC	TIC	pH	DM
	--- mg L^{-1} ---							%
Dairy slurry	1,158±24	192±6	540±2	344±3	13,122±1,250	46±9	6.75±0.06	10.08±0.16
Pig slurry	3,689±119	3,364±15	199±3	137±1	4,896±130	236±105	7.95±0.07	2.21±0.11
Dairy soiled water	105±2	76.8±0.6	15.4±0.2	14.1±0.1	602±7	169±2	7.14±0.07	0.28±0.01

4.3.2 Leachate flow, phosphorus and pH

The weekly average volume of leachate (weeks 10 – 28) collected from all columns following the acclimatization period (weeks 1 – 9) had a high leachate to irrigation ratio (98.1±7.4%) and all columns remained free draining, indicating steady-state flow conditions throughout the experiment. There were no soil P losses measured in the leachate for all treatments, reflective of the very low proportions of P applied in the slurries compared to the net P storage capacity of the soil (1.9, 0.8 and 0.1% for dairy and pig slurries and DSW, respectively), the low soil P content, and the removal of soil macropore networks in the packed columns (van Es et al., 2004). The average pH of the leachate remained constant for all treatments (8.38±0.16) throughout the study.

4.3.3 Leachate Nitrogen

Total N in the control soil leachate increased (3.6 to 23.8 mg column^{-1}, equivalent to 4 to 28 kg ha^{-1}) rapidly during the first three weeks of the acclimatization period (weeks 1 – 9) and then declined steadily in the following six weeks, where it remained constant at an average flux of 2.5±1.2 kg ha^{-1} for the remainder of the experiment. This initial increase and subsequent decrease was also observed to occur for NO_3-N in the control soil leachate (Fig. 4.3). The effect of wetting dry soil is well known to result in short lived pulses of C and N mineralisation (Borken and Matzner, 2009), which can exceed those of permanently moist soils and persist for several weeks (Beare et al., 2009).

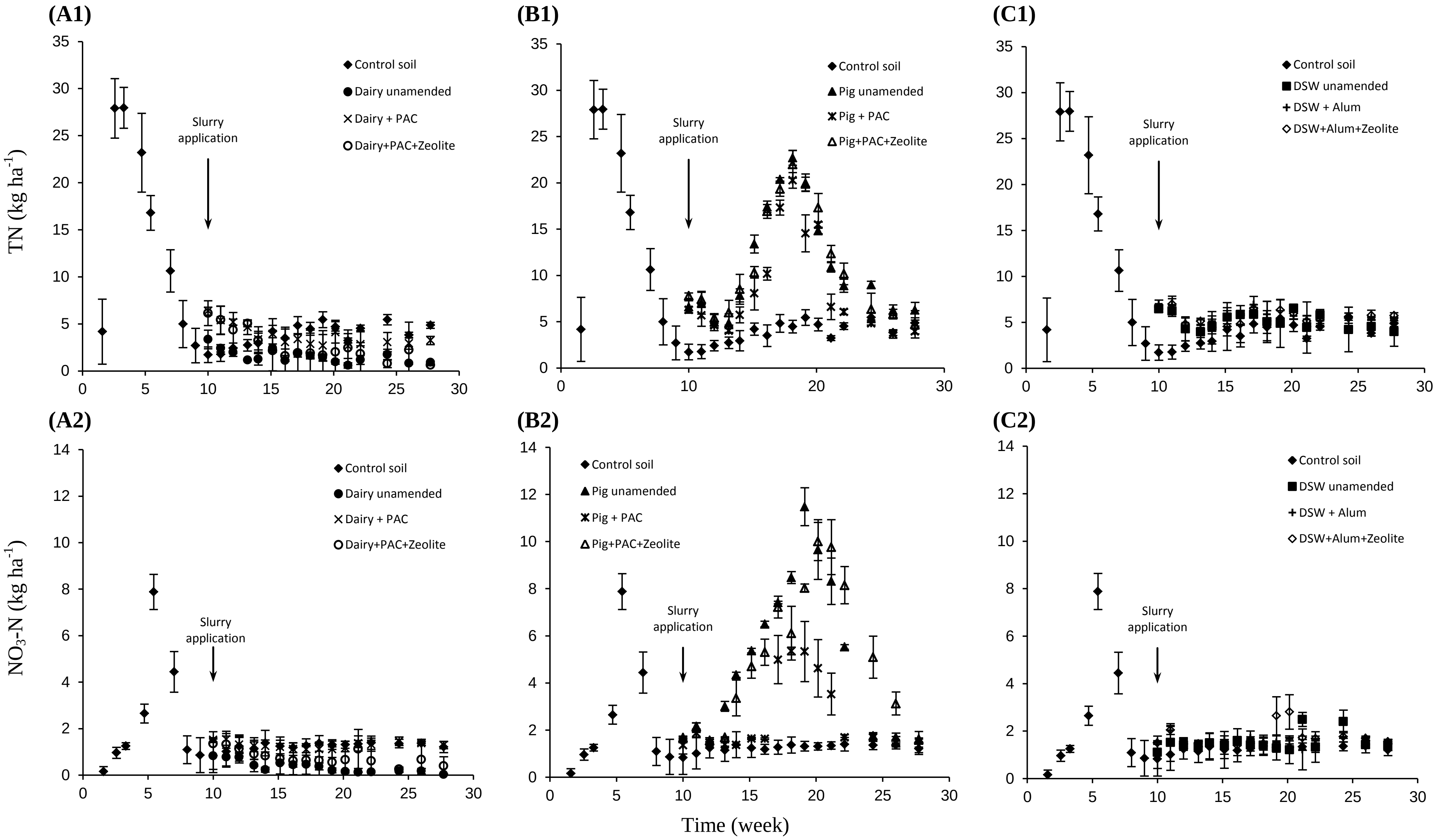

Figure 4.3 Average (n=3) weekly fluxes of total N (TN) and nitrate (NO_3-N) for dairy slurry (A1 – A2), pig slurry (B1 – B2) and dairy soiled water (DSW) (C1 – C2). Error bars indicate SD.

Application of unamended and amended pig slurries in week 10 resulted in increased TN fluxes between weeks 14 and 24, peaking between 20 and 22 kg ha^{-1} for all treatments at week 18 (Fig. 4.3 – B1). There were similar increases in NO_3-N during the same period, which formed on average 39.4% of TN for all slurries and all treatments (Fig. 4.3 – B2). These leaching losses were lower than those reported by Bolado-Rodríguez et al. (2010) in a soil column experiment to measure the effect of N and TOC leaching from surface applied raw and air stripped pig slurries irrigated with $CaCl_2$ solution at a constant rate equivalent to 1.7 mm h^{-1} and slightly lower than those reported by Troy et al. (2014), who measured peak amounts of NO_3-N in week 18 equivalent to *c.* 14 kg ha^{-1} in leachate from a tillage soil mixed with pig manure biochar. The high NO_3-N losses from pig slurry reflect the large proportion (91%) of mineral N (predominantly NH_4-N) in the applied slurry (Table 4.2), which can be quickly converted to NO_3.

There were no significant differences between treatments for pig slurries for TN and between unamended pig slurry and pig slurry amended with zeolite and PAC for NO_3-N in leachate; however, pig slurry amended with PAC had lower cumulative TN and NO_3-N fluxes than unamended pig slurry and pig slurry amended with PAC and zeolite (Fig. 4.4, Table 4.3). This is consistent with the findings of O’ Flynn et al. (2013), who also found no significant differences in leachate N and C from unamended and PAC-amended pig slurries in a soil column experiment. The reduced leachate N and NO_3-N fluxes from PAC-amended pig slurry may be due, in part at least, to the flocculation of N-enriched slurry particles on the upper levels of the soil surface, reducing their migration through the soil. Addition of zeolite to the pig slurry may have accelerated organic degradation (Zhang et al., 2016) and contributed to the mineralisation of N to NH_4-N, thereby increasing NO_3-N concentrations in the leachate.

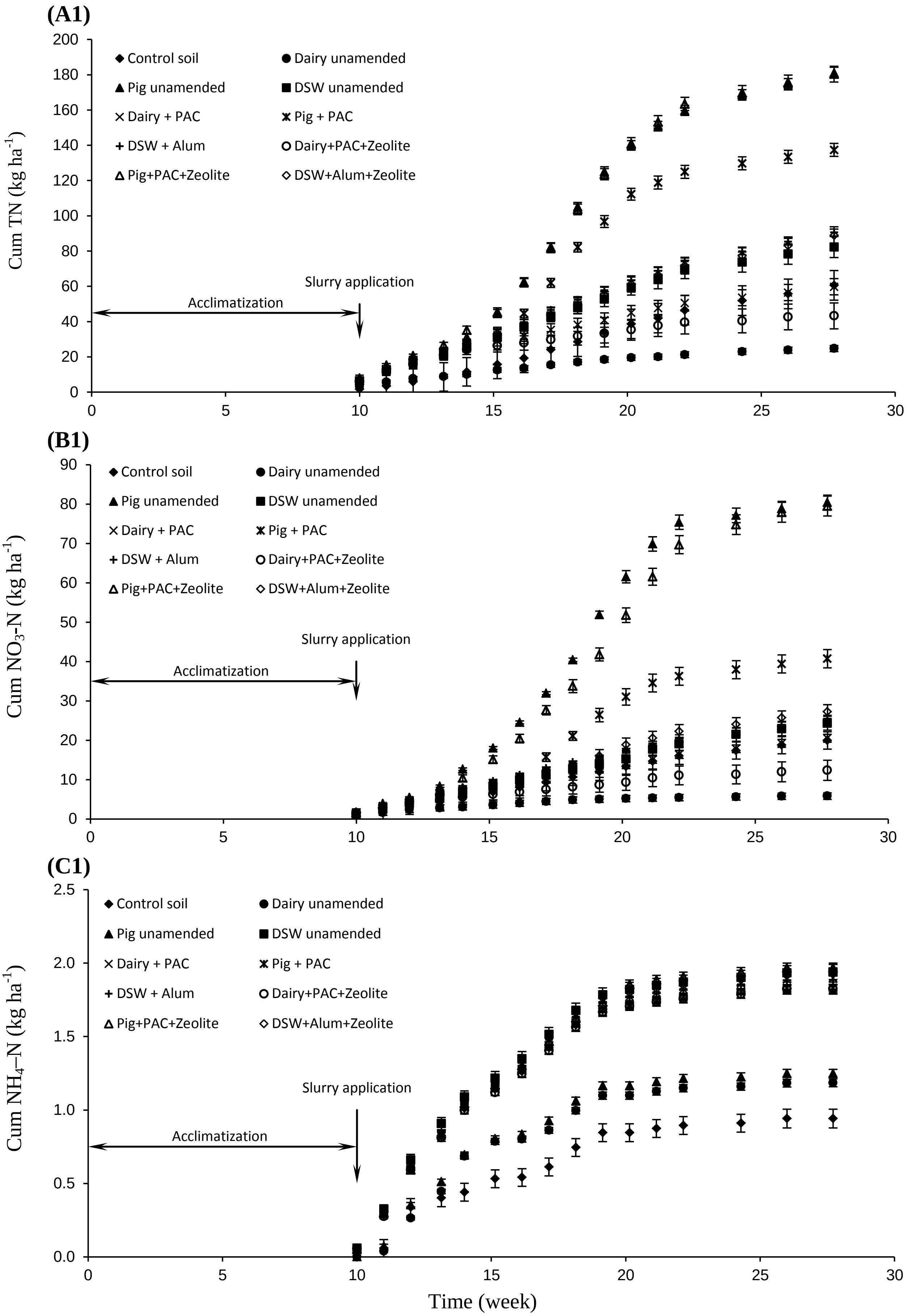

Figure 4.4 Average cumulative fluxes of total N (TN), nitrate (NO_3-N) and ammonium (NH_4-N) for control soil and all unamended and amended slurries (A1, B1 and C1). Error bars indicate SD.

Table 4.3 Average (n=3) leachate flux (kg ha^{-1}) over the indicated time intervals for total N (TN), ammonium (NH_4-N) and nitrate (NO_3-N) from control soil, unamended and amended dairy and pig slurries, and dairy soiled water (DSW).

		Treatment									
Parameter (kg ha^{-1})	Week*	Control soil	D(U)	D(C)	D(C+Z)	P(U)	P(C)	P(C+Z)	DSW(U)	DSW(C)	DSW(C+Z)
TN	10 – 13	8.64^{a}	8.90^{a}	21.59^{b}	20.94^{b}	23.42^{b}	20.60^{b}	26.61^{b}	20.99^{b}	23.22^{b}	23.59^{b}
	14 – 17	15.46^{ab}	6.60^{a}	13.71^{ab}	8.88^{a}	59.02^{c}	41.33^{bc}	55.10^{c}	21.85^{ab}	23.31^{ab}	20.30^{ab}
	18 – 21	17.85^{a}	4.60^{a}	12.33^{a}	7.99^{a}	68.40^{b}	56.94^{b}	71.56^{b}	20.92^{a}	22.24^{a}	22.59^{a}
	22 – 25	9.98^{bcd}	2.91^{ab}	5.91^{abc}	2.62^{a}	17.88^{e}	10.90^{cde}	16.53^{de}	10.03^{bcd}	11.09^{cde}	10.89^{cde}
	26 – 28	8.68^{cde}	1.73^{a}	6.19^{bc}	2.84^{ab}	12.51^{f}	7.62^{cd}	10.55^{def}	8.53^{cde}	10.72^{def}	11.51^{ef}
NH_4-N	10 – 13	0.40^{a}	0.45^{a}	0.84^{a}	0.81^{a}	0.51^{a}	0.83^{a}	0.84^{a}	0.91^{a}	0.84^{a}	0.83^{a}
	14 – 17	0.21^{a}	0.42^{ab}	0.64^{b}	0.59^{ab}	0.32^{ab}	0.60^{ab}	0.63^{b}	0.61^{ab}	0.63^{b}	0.60^{ab}
	18 – 21	0.26^{a}	0.26^{a}	0.32^{a}	0.33^{a}	0.27^{a}	0.32^{a}	0.42^{a}	0.33^{a}	0.32^{a}	0.33^{a}
	22 – 25	0.04^{a}	0.03^{a}	0.06^{a}	0.05^{a}	0.03^{a}	0.06^{a}	0.05^{a}	0.05^{a}	0.05^{a}	0.05^{a}
	26 – 28	0.03^{a}	0.03^{a}	0.04^{a}	0.04^{a}	0.02^{a}	0.03^{a}	0.03^{a}	0.04^{a}	0.03^{a}	0.03^{a}
NO_3-N	10 – 13	4.23^{ab}	2.78^{a}	5.62^{bc}	4.70^{abc}	8.32^{d}	6.08^{bcd}	7.07^{cd}	5.40^{abc}	6.54^{bcd}	6.47^{bcd}
	14 – 17	5.07^{ab}	1.66^{a}	4.69^{ab}	2.79^{ab}	23.63^{c}	9.64^{b}	20.59^{c}	5.94^{ab}	6.34^{ab}	5.44^{ab}
	18 – 21	5.33^{ab}	0.86^{a}	4.75^{ab}	2.96^{ab}	37.94^{d}	18.84^{c}	33.91^{d}	6.41^{ab}	5.95^{ab}	8.64^{b}
	22 – 25	2.75^{a}	0.31^{a}	2.77^{a}	0.86^{a}	7.29^{ab}	3.38^{a}	13.24^{b}	3.73^{a}	3.37^{a}	3.46^{a}
	26 – 28	2.58^{abc}	0.20^{a}	2.66^{abc}	1.06^{ab}	3.26^{bc}	2.81^{bc}	4.73c	2.84^{bc}	3.24^{bc}	3.26^{bc}

D(U), unamended dairy slurry; D(C), dairy slurry amended with polyaluminum chloride (PAC) at 12.8 kg t^{-1}; D(C+Z), dairy slurry amended with zeolite at 202 kg t^{-1} and PAC at 12.8 kg t^{-1}; DSW(U), unamended dairy soiled water; DSW(C), dairy soiled water amended with alum at 1.0 kg t^{-1}; DSW(C+Z), dairy soiled water amended with zeolite at 28 kg t^{-1} and alum at 1.0 kg t^{-1}; P(U), unamended pig slurry; P(C), pig slurry amended with PAC at 3.8 kg t^{-1}; P(C+Z), pig slurry amended with zeolite at 133 kg t^{-1} and PAC at 3.8 kg t^{-1}. Slurry surface application rates were 39, 46 and 50 t ha^{-1} for dairy and pig slurries, and DSW respectively.

*Weeks 1 – 9 represent soil acclimatization period for all columns. All slurries were surface applied on week 10.

^{abc}Values in each row followed by the same letters are not statistically different ($\rho < 0.05$).

In general, application of unamended and amended dairy slurries did not significantly increase leachate TN (average 2.7±1.8 kg ha^{-1} across all treatments) and NO_3-N (average 0.8±0.6 kg ha^{-1} across all treatments) fluxes above those of the control soils, and while there were no significant differences between treatments between weeks 14 and 28, TN losses were higher from amended slurries between weeks 10 and 13 (Fig. 4.3 – A1 and A2; Table 4.3). Similarly, application of unamended and amended DSW did not increase TN and NO_3-N fluxes above those of the control soil and treatments were not significantly different from each other (Fig. 4.3 – C1 and C2, Table 4.3). These relatively low N leaching losses from dairy slurry were consistent with the relatively small amount (16.5%) of mineral N (mainly as NH_4-N) as a proportion of TN in the applied slurry (Table 4.2) and are consistent with the findings of Di et al. (1998), who measured dairy slurry leaching losses of 8 – 25 kg NO_3-N ha^{-1} y^{-1} in a lysimeter study comparing dairy slurry with inorganic fertilizer applications. The mineralisation of the organic N load in the applied dairy slurries is influenced by variations in soil, weather, manure composition and management (van Es et al., 2006), and is quite a slow process, likely to extend beyond the experimental period of this study. It is likely, therefore, that repeated applications of dairy slurry over a longer timescale may result in higher amounts of leachate NO_3-N (Kayser et al., 2015) than were observed during the current study.

Cumulative NH_4-N in leachate was highest for pig slurry amended with PAC and zeolite (1.97 kg ha^{-1}) and was tightly grouped with all other amended treatments and with unamended DSW (Fig. 4.4 – C1). The cumulative amounts of NH_4-N leached from unamended pig and dairy slurries (1.25 and 1.19 kg ha^{-1}, respectively) were lower than those of DSW, but remained above those of the control soil (0.94 kg ha^{-1}). This further illustrates the ability of amended and unamended pig slurry, which had by far the highest NH_4-N concentration of the three applied slurries (Table 4.2), to nitrify in significant quantities, with consequent high levels of NO_3-N in leachate. Ammonium-N leachate losses from dairy slurry are limited by the relatively low amounts of NH_4-N in the applied slurries (Table 4.2) and may also be affected by the moderately high CEC (10.9 cmol kg^{-1}) of the soil. The higher NH_4-N losses from DSW were reflective of its high NH_4-N/TN ratio (73%) and its inability to nitrify to the same extent as pig slurry, which may have been affected by its relatively high C/N ratio (7.3).

A mass balance to estimate the relative cumulative amounts of slurry N leached (weeks 10 – 28) was carried out using:

$$\%\ \text{N leached} = \frac{(\sum \text{Mass N}_{\text{leachate}} - \sum \text{Mass N}_{\text{control soil}})}{\sum \text{N}_{\text{applied slurry}}} \qquad (2)$$

where: $\sum$ Mass $\text{N}_{\text{leachate}}$ is the cumulative mass of TN measured in the leachate; $\sum$ Mass $\text{N}_{\text{control soil}}$ is the cumulative mass of TN leached from the control soil and $\sum$ $\text{N}_{\text{applied slurry}}$ is the TN of the applied slurry, calculated by multiplying the applied slurry volume by its concentration. All of the TN in the DSW was leached for all treatments; however, the amount of TN in DSW was very low when compared with either pig or dairy slurries (Table 4.2). Approximately 70% of TN from unamended pig slurry and pig slurry amended with PAC and zeolite was leached, and this reduced to 45% for pig slurry amended with PAC. None of the TN in the dairy slurries (all treatments) was leached, and this was reflected in the insignificant differences in N leaching between the dairy slurries (unamended and amended) and the control soil between weeks 14 and 28 (Table 4.3). This finding supports the observation that the relatively low fraction of plant available N in dairy slurry combined with its high DM content (10%) and with the relatively high CEC of the soil reduces its overall potential for leaching and is consistent with the findings of Salazar et al. (2012), who, in a field experiment to compare the effects of dairy slurry application on N leaching losses with those from inorganic fertilizer, reported cumulative net N leaching losses < 1% of the applied slurry N, which comprised *c.* 65% organic N. The higher C/N ratio of the dairy slurry (11.4±1.3) also indicates that it will have a slower mineralisation process than either pig slurry (1.4±0.0) or DSW (7.3±0.2) (Table 4.2).

Total N and N_{org} in leachate were dominated by their respective dissolved forms for all slurries. Total dissolved N as a proportion of TN was highest for pig slurries (91%, 92% and 96% for unamended pig slurry, pig slurry amended with PAC and pig slurry amended with PAC and zeolite, respectively) followed by DSW (90%, 96% and 96% for unamended DSW, DSW amended with alum and DSW amended with alum and zeolite, respectively). The average proportion of TN_{d} to TN for dairy slurry (82%) was closest to that of the control soil (72%), supporting the evidence that most of the N leached from the dairy slurry columns was from the soil and not the applied slurry. Dissolved organic N as a proportion of N_{org} was highest for DSW (86%, 94% and 94% for unamended DSW, DSW amended with alum and DSW amended with alum and zeolite, respectively), followed by pig slurries (84%, 89% and 93% for unamended pig slurry, pig slurry amended with PAC and pig slurry amended with PAC and zeolite, respectively). However the average cumulative amount of DON leached from pig slurries (86.3 kg ha^{-1}) was considerably higher than that for DSW (54.3 kg ha^{-1}) and dairy slurries (21 kg ha^{-1}).

4.3.4 Leachate Carbon

The average cumulative TOC leached from unamended dairy slurry (82 kg ha^{-1}) was significantly higher than that from the control soil and from all other unamended and amended slurries which were not significantly different from each other, ranging from 48.2 to 35.6 kg ha^{-1} for PAC amended pig slurry and DSW amended with alum and zeolite, respectively (Fig. 4.5, Table 4.4). This is reflective of the much higher TOC concentrations in the dairy slurry compared to pig slurry and DSW (Table 4.2). The average cumulative TOC loads for unamended and amended pig slurries were lower than those reported by O’ Flynn et al. (2013), who measured leachate loads equivalent to *c.* 75 kg TOC and 240 kg TIC ha^{-1} in an 8 month soil column experiment. Dairy slurry amended with PAC and with PAC and zeolite significantly reduced leachate TOC concentrations compared to unamended dairy slurry (Table 4.4). This was most likely due to the flocculation of the C-enriched dairy slurry particles at the soil surface by the PAC combined with small amounts of TOC adsorbed by the zeolite (Murnane et al., 2016). Total organic C fluxes were dominated by DOC, with average DOC/TOC ratios of 76% for control soil, 83% for unamended and amended dairy slurries, 75% for unamended and amended pig slurries, and 82% for unamended and amended DSW. The average amounts of TOC leached from unamended and amended slurries over the duration of the experiment, compared with the amounts applied (Eqn. 2), were negligible for both pig slurry and DSW (<1%), but were also very low for dairy slurry (average 2.5%).

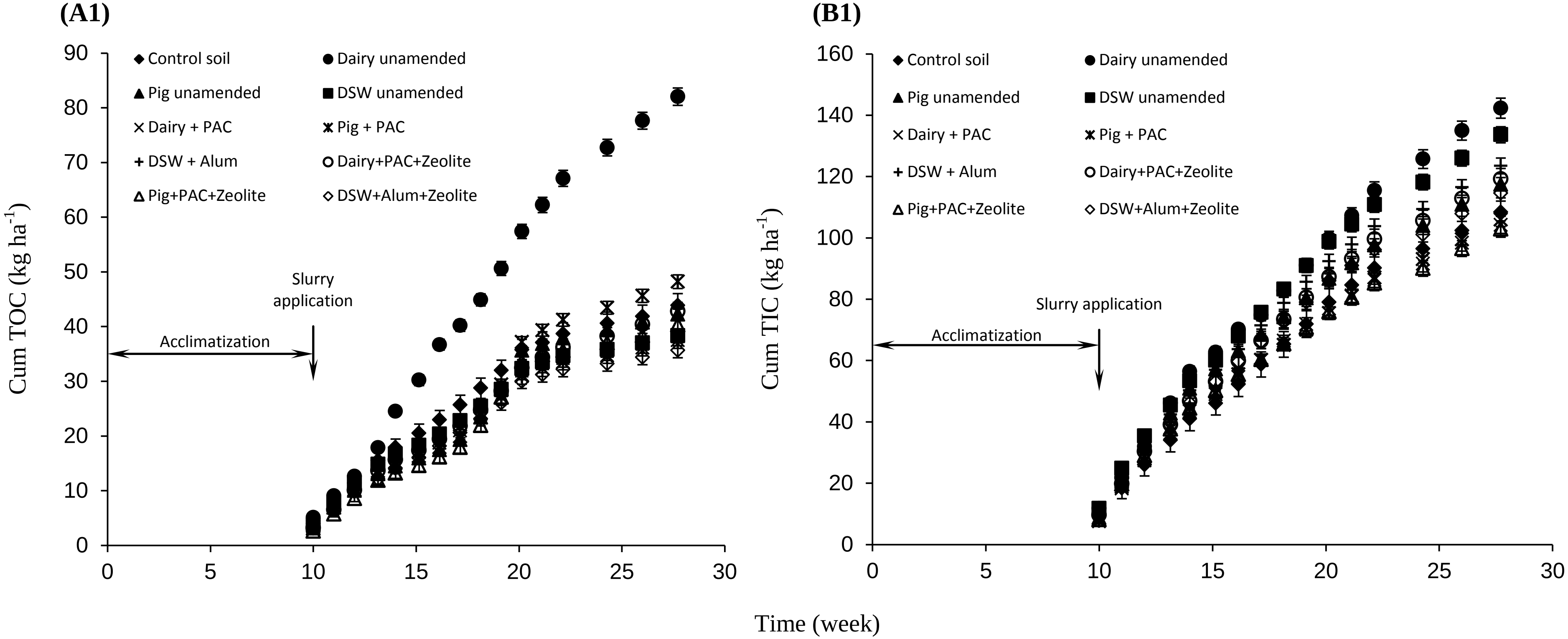

Figure 4.5 Average (*n*=3) cumulative fluxes of total organic C (A1) and total inorganic C (B1) for control soil and all unamended and amended slurries. Error bars indicate SD.

Table 4.4 Average (n=3) leachate flux (kg ha^{-1}) over the indicated time intervals for total organic C (TOC) and total inorganic C (TIC) from control soil, unamended and amended dairy and pig slurries and dairy soiled water (DSW).

		Treatment									
Parameter (kg ha^{-1})	Week*	Control soil	D(U)	D(C)	D(C+Z)	P(U)	P(C)	P(C+Z)	DSW(U)	DSW(C)	DSW(C+Z)
TOC	10 – 13	15.49^{bc}	17.87^{c}	13.36^{ab}	13.63^{ab}	13.05^{ab}	13.54^{ab}	11.89^{a}	14.85^{abc}	13.56^{ab}	12.07^{a}
	14 – 17	10.17^{a}	22.31^{b}	7.60^{a}	8.21^{a}	6.27^{a}	6.37^{a}	6.02^{a}	7.93^{a}	8.15^{a}	8.50^{a}
	18 – 21	11.40^{a}	22.06^{a}	11.33^{a}	12.55^{a}	17.55^{a}	19.43^{a}	16.92^{a}	10.75^{a}	10.48^{a}	10.61^{a}
	22 – 25	3.51^{ab}	10.49^{c}	2.43^{ab}	3.83^{ab}	2.54^{ab}	4.11^{b}	2.16^{a}	2.28^{ab}	2.24^{ab}	2.00^{a}
	26 – 28	3.30^{abc}	9.31^{d}	2.79^{ab}	4.57^{bc}	2.84^{abc}	4.76^{c}	3.31^{abc}	2.55^{a}	2.71^{ab}	2.45^{a}
TIC	10 – 13	34.02^{a}	46.09^{a}	36.41^{a}	39.09^{a}	42.86^{a}	37.98^{a}	37.63^{a}	45.40^{a}	42.34^{a}	38.65^{a}
	14 – 17	24.72^{a}	28.74^{a}	23.67^{a}	27.31^{a}	25.61^{a}	22.20^{a}	22.70^{a}	30.29^{a}	29.05^{a}	27.47^{a}
	18 – 21	25.84^{abc}	32.45^{d}	21.14^{ab}	26.69^{bcd}	23.35^{abc}	20.77^{ab}	20.21^{a}	28.75^{cd}	26.47^{bcd}	24.84^{abc}
	22 – 25	11.89^{ab}	18.42^{c}	10.31^{ab}	12.53^{ab}	12.17^{ab}	12.13^{ab}	9.54^{a}	13.75^{b}	11.51^{ab}	10.12^{ab}
	26 – 28	11.93^{a}	16.58^{b}	12.72^{ab}	13.58^{ab}	13.50^{ab}	12.86^{ab}	12.80^{ab}	15.45^{ab}	14.08^{ab}	13.49^{ab}

All treatments are described in Table 4.3.

*Weeks 1 – 9 represent soil acclimatization period for all columns. All slurries were surface applied on week 10.

^{abc}Values in each row followed by the same letters are not statistically different ($\rho < 0.05$).

The average cumulative TIC leached from all slurries and from the control soil was much higher than the corresponding TOC fluxes (Fig. 4.5), with the highest load from unamended dairy slurry (142.3 kg ha^{-1}) and the lowest from pig slurry amended with PAC and zeolite (102.9 kg ha^{-1}). All unamended and amended slurry applications resulted in higher TIC leachate fluxes than the control soil except for pig slurry amended with PAC, pig slurry amended with PAC and zeolite, and dairy slurry amended with PAC; however, these differences were not significant (Table 4.4). There were significant reductions in leachate TIC (weeks 22-25) from dairy slurry amended with PAC and dairy slurry amended with PAC and zeolite compared to unamended dairy slurry, likely due to flocculation by PAC of C enriched dairy slurry, but there were no significant differences between unamended and amended pig slurries and unamended and amended DSW (Table 4.4).

All of the applied TIC from the dairy slurries and DSW and an average 28% from the pig slurries, which had the highest concentration of TIC (Table 4.2), was leached (Eqn. 2) over the experimental duration, indicating the greater mobility of the mineralised C and its potential for leaching.

4.3.5 Greenhouse gas emissions after land application

Emissions of CO_2-C from unamended pig slurry were highest on the day of slurry application (4.0±0.3 kg CO_2-C ha^{-1} h^{-1}) and reduced quickly between days 1 and 8, where they remained constant (average 1.0±0.3 kg CO_2-C ha^{-1} h^{-1}) until the end of the sampling period (Fig. 4.6 – A1). This is reflective of the high TIC in leachate from pig slurry, which can result in increased microbial activity and CO_2 emissions (Cayuela et al., 2010). Slight, but insignificant increases in emissions from pig slurries were observed immediately after irrigation of the columns on days 5, 8 and 12 (Fig. 4.6 – A1), indicating that disturbance of surface applied slurries as well as change on soil moisture can result in increased CO_2 emissions (Huang et al., 2017). A similar pattern of increased, but lower, CO_2-C emissions than from pig slurries were observed for dairy slurries (1.2±0.2 kg CO_2-C ha^{-1} h^{-1}) and DSW (1.1±0.1 kg CO_2-C ha^{-1} h^{-1}) on the day of slurry application, followed by quick reductions between days 1 and 8 to averages of 0.3±0.0 and 0.6±0.1 kg CO_2-C ha^{-1} h^{-1}, respectively (results not displayed).

Average cumulative CO_2-C emissions averaged across all treatments of unamended and amended slurries were highest for pig slurries (680±63 kg CO_2-C ha^{-1}), followed by DSW (515±59 kg CO_2-C ha^{-1}) and dairy slurries (486±215 kg CO_2-C ha^{-1}), and were all greater than those from the control soils (137±3 kg CO_2-C ha^{-1}) over the experimental duration (Fig. 4.6 – A2). This is consistent with the findings of O' Flynn et al. (2013), who measured cumulative CO_2 emissions between *c.* 500 and 850 kg CO_2-C ha^{-1} from unamended and PAC-amended pig slurries. The CO_2 emissions from dairy slurries were similar to those measured by Brennan et al. (2015) (450 kg CO_2-C ha^{-1}) in a laboratory-scale study to evaluate the impact of chemical amendments on GHG emissions. There were no statistical differences in cumulative CO_2 emissions between unamended and amended pig slurries or between unamended and amended DSW; however, dairy slurry amended with PAC and dairy slurry amended with PAC and zeolite, while not significantly different from each other, resulted in higher CO_2-C emissions than from unamended dairy slurry, which was not significantly different from the control soil (Table 4.5). This supports our earlier observation that C-enriched dairy slurry particles may have flocculated on the soil surface when amended with either PAC or PAC and zeolite, with the concomitant increase in CO_2 releases when compared with unamended dairy slurry.

There were no CH_4 emissions from the control soil or applied slurries except from unamended pig slurry, pig slurry amended with PAC, and pig slurry amended with PAC and zeolite on day 1 (0.101±0.008, 0.084±0.009 and 0.106±0.011 kg CH_4-C ha^{-1} h^{-1}, respectively) and day 2 (0.013±0.002, 0.007±0.004 and 0.014±0.001 kg CH_4-C ha^{-1} h^{-1}, respectively) (results not displayed). This response to treatment was also noted by Sistani et al. (2010), who, in a field experiment to measure GHG emissions from pig slurry by different application methods, reported elevated CH_4 fluxes compared with the soil control for 3 to 5 d after application with very low or zero emissions thereafter. In the current study, no CH_4 emissions were detected from either untreated or treated pig slurries after day 2, as oxic conditions prevailed over the preferred anoxic conditions required for CH_4 production, and there were no significant differences between the treatments.

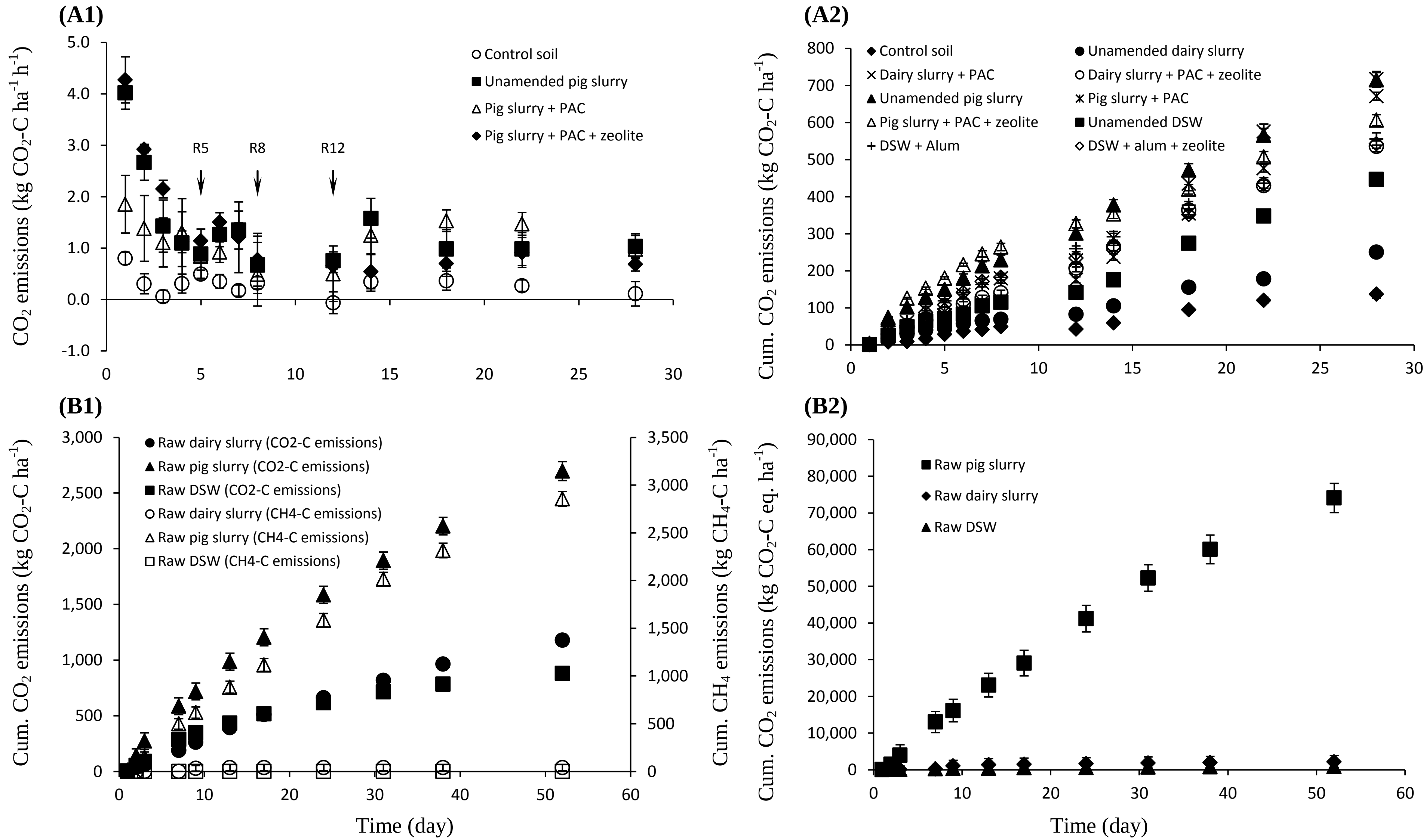

Figure 4.6 Average CO_2 emissions from control soil and from soil applied unamended and amended pig slurries with irrigation on days 5, 8 and 12 (R5, R8 and R12) indicated **(A1)**; average cumulative CO_2 emissions from control soil and from all unamended and amended slurries **(A2)**; average cumulative CO_2 and CH_4 emissions from stored undisturbed raw dairy and pig slurries and DSW **(B1)**, and average cumulative total equivalent CO_2 emissions (comprising CO_2 and CH_4) from stored undisturbed raw dairy and pig slurries and DSW (1 CH_4 = 25 CO_2 eq.) **(B2)**. Error bars indicate SD, *n*=3.

Table 4.5 Average cumulative CO_2 emissions and % increase from control soil, and average cumulative methane (CH_4) emissions (*n*=3).

Treatment	Cum CO_2 emissions (kg CO_2-C ha^{-1})	% increase	Cum CH_4 emissions (kg CH_4-C ha^{-1})
Control soil	137^{a}	-	-
D(U)	251^{a}	83	-
D(C)	671^{cd}	391	-
D(C+Z)	536^{bc}	292	-
P(U)	715^{d}	423	2.73^{a}
P(C)	717^{d}	425	2.18^{a}
P(C+Z)	606^{cd}	344	2.90^{a}
DSW(U)	447^{b}	227	-
DSW(C)	556^{bc}	307	-
DSW(C+Z)	543^{bc}	297	-

Cum. emission values in a column followed by the same letters are not statistically different ($\rho < 0.05$). All treatments are described in Table 4.3.

4.3.6 Greenhouse gas emissions during storage

Emissions of CO_2 from stored raw undisturbed dairy and pig slurries, and DSW were highest on day 1 (3.25±0.07, 9.90±0.12 and 3.72±0.08 kg CO_2-C ha^{-1} h^{-1}, respectively) and reduced rapidly between days 1 and 10 to averages of 0.99±0.26, 2.08±0.46 and 0.61±0.24 kg CO_2-C ha^{-1} h^{-1} between days 13 and 52 (results not displayed). Cumulatively, raw pig slurry emitted the highest quantity of CO_2 (2,698±85 kg CO_2-C ha^{-1}), followed by dairy slurry (1,179±53 kg CO_2-C ha^{-1}) and DSW (882±51 kg CO_2-C ha^{-1}) (Fig. 4.6 – B1).

Raw pig slurry had the highest cumulative CH_4 emissions (2,856±78 kg CH_4-C ha^{-1}), with much lower emissions from dairy slurry (40±32 kg CH_4-C ha^{-1}) and no emissions from DSW (Fig. 4.6 – B1). The cumulative CO_2-C eq. emissions (comprising CO_2-C and CH_4-C) based on the predicted 100 yr. global warming potential (GWP_{100}) of 25 CO_2 eq. for 1 CH_4 (IPCC, 2007) were much higher from stored raw pig slurry (74,100±3,972 kg CO_2-C eq. ha^{-1}) than from either dairy slurry (2,177±1,693 kg CO_2-C eq. ha^{-1}) or DSW (882±512 kg CO_2-C eq. ha^{-1}) (Fig. 4.6 – B2). The average CH_4 fluxes for pig and dairy slurries, respectively, were 338 and

9.2 mg m^{-2} h^{-1} and accounted for 46 and 96% of the total CO_2 eq. emissions. In an investigation into CO_2 and CH_4 emissions from pig manure storage facilities, Na et al. (2008) measured similar average CH_4 emissions of 306 mg m^{-2} h^{-1} with CH_4 contributing *c*. 95% of the total CO_2 eq. emissions. In a study to measure GHG emissions from stored dairy slurry on multiple farms, Le Richie et al. (2016) reported emissions ranging from 6.3 – 25.9 g CH_4 m^{-2} d^{-1} at average air temperatures of 18 °C. The high CO_2 eq. emissions from stored slurries, in particular pig slurry (Fig. 4.6 – B2), highlights the need to consider storage emissions when assessing GHG emissions from agricultural slurries (Rodhe et al., 2015).

4.3.7 Measurement of overall environmental impact of treatments

The overall impact of each treatment is shown in Table 4.6. Of the treatments examined, unamended and chemically amended pig slurry had the highest cumulative CO_2 and CH_4 emissions and leaching losses of N and C. Although the dual amendment of zeolite and PAC/alum proved successful in reducing surface runoff losses of N, P and C (Murnane et al., 2016), they did not mitigate leaching losses and GHG emissions from soil columns and, moreover, actually increased contamination (gaseous and water) from the soil columns in the case of dairy slurry and DSW.

Table 4.6 Measurement of overall environmental impact of treatments in terms of cumulative total N (TN), total C [total organic C (TOC) and total inorganic C (TIC)] losses (kg ha^{-1}) and cumulative carbon dioxide (CO_2) and methane (CH_4) emissions (expressed as kg CO_2-C eq. ha^{-1}). (1 CH_4 = 25 CO_2 eq.)

Slurry type	Treatment	TN	TOC	TIC	$CO_2 + CH_4$	Total
		--------------- kg ha^{-1} ---------------			(kg CO_2-C eq. ha^{-1})	
Dairy	Unamended	25	82	142	251	500
	+PAC	60	38	104	671	873
	+PAC and zeolite	43	43	119	536	741
Pig	Unamended	181	42	117	740	1,081
	+PAC	137	48	106	737	1,028
	+PAC and zeolite	180	40	103	633	956
DSW	Unamended	82	38	134	447	701
	+alum	91	37	123	556	807
	+alum and zeolite	89	36	115	543	782

4.4 Conclusions

Of the three slurries examined, pig slurry has the greatest potential for N leaching to groundwater because of its high N concentrations, high proportion of mineral N, and ability to nitrify. The study found that N leaching from DSW is less likely than from pig slurry, given its typically lower N concentrations and higher C/N ratio. Application of amendments to slurries had no impact on C leaching or on CO_2 and CH_4 emissions except for dairy slurries, where PAC only and PAC and zeolite-amended dairy slurries reduced the amounts of TOC and TIC leached, but increased CO_2 emissions compared to unamended dairy slurry.

The column experiment used in this study represented a worst case scenario of winter slurry application (on bare soil with no crop growth) followed by persistent rainfall. While zeolite and PAC amendments were previously shown to be effective in mitigating surface runoff losses of N, P and C, particularly from dairy slurry, these benefits may be offset by their deleterious impact on leaching and CO_2 emissions. The combined N and C leaching and gaseous losses were highest for pig slurry, and this would seem to pose the greatest short term environmental threat of the three slurries examined.

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Chapter 5

The focus of the studies described in chapters 2, 3 and 4 was on measuring surface and leaching losses of nitrogen (N), phosphorus (P), carbon (C) and suspended solids (SS), and carbon dioxide (CO_2) and methane (CH_4) gas emissions from amended and unamended dairy and pig slurries, and dairy soiled water (DSW) which were surface applied to the soil. In the laboratory-based study described in this chapter, the treatment of DSW using intermittently loaded sand and woodchip filters is examined. In particular, this study reports on the impact of filter depth and organic loading rate when using woodchip media, and evaluates the effectiveness of sand and woodchip media to passively treat DSW. This chapter addresses the third and final hypothesis of the thesis, which states that intermittently loaded filters using woodchip media are more effective than those using sand media when treating DSW.

The contents of this chapter have been published in Water Research *(2016; 103: 408-415)*. John Murnane developed the experimental design, with inputs from Drs. Mark G. Healy and Ray Brennan. John Murnane set up the experiment, carried out all of the testing and analysis, and is the primary author of this publication. Dr. Mark G. Healy was the main contributor to editing the paper with inputs from Prof. Owen Fenton and Dr. Ray Brennan. John Murnane carried out all of the statistical analysis with review provided by Dr. Ray Brennan. The published paper is included in Appendix C.

Assessment of intermittently loaded woodchip and sand filters to treat dairy soiled water

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Abstract

Land application of dairy soiled water (DSW) is expensive relative to its nutrient replacement value. The use of aerobic filters is an effective alternative method of treatment and potentially allows the final effluent to be reused on the farm. Knowledge gaps exist concerning the optimal design and operation of filters for the treatment of DSW. To address this, 18 laboratory-scale filters, with depths of either 0.6 m or 1 m, were intermittently loaded with DSW over periods of up to 220 days to evaluate the impacts of depth (0.6 m versus 1 m), organic loading rates (OLRs) (50 versus 155 g COD $m^{-2}d^{-1}$), and media type (woodchip versus sand) on organic, nutrient and suspended solids (SS) removals. The study found that media depth was important in contaminant removal in woodchip filters. Reductions of 78% chemical oxygen demand (COD), 95% SS, 85% total nitrogen (TN), 82% ammonium-nitrogen (NH_4-N), 50% total phosphorus (TP), and 54% dissolved reactive phosphorus (DRP) were measured in 1 m deep woodchip filters, which were greater than the reductions in 0.6 m deep woodchip filters. Woodchip filters also performed optimally when loaded at a high OLR (155 g COD m^{-2} d^{-1}), although the removal mechanism was primarily physical (i.e. straining) as opposed to biological. When operated at the same OLR and when of the same depth, the sand filters had better COD removals (96%) than woodchip (74%), but there was no significant difference between them in the removal of SS and NH_4-N. However, the likelihood of clogging makes sand filters less desirable than woodchip filters. Using the optimal designs of both configurations, the filter area required per cow for a woodchip filter is more than four times less than for a sand filter. Therefore, this study found that woodchip filters are more economically and environmentally effective in the treatment of DSW than sand filters, and optimal performance may be achieved using woodchip filters with a depth of at least 1 m, operated at an OLR up to 155 g COD m^{-2} d^{-1}.

5.1 Introduction

Dairy soiled water (DSW) (variously referred to as dairy effluent (Longhurst et al., 2000; McFarland et al., 2003), dairy dirty water (Cannon et al., 2000; Moir et al., 2005), or milk-house washwater (Joy et al., 2001)), is a variable strength dairy effluent (typical range 1000 – 10000 mg 5-day biochemical oxygen demand (BOD_5) L^{-1}) comprising milking parlour and holding area washings generated in large but variable volumes (27 – 148 L cow^{-1} d^{-1}), and is characterised by low dry matter (DM) content (typically < 3 - 4%). Nutrient concentrations in DSW vary considerably, typically between 70 to 500 mg total nitrogen (TN) L^{-1} and 20 to >100 mg total phosphorus (TP) L^{-1} (Minogue et al., 2015). The volume and strength of DSW is seasonal and depends on farm management practices, including the efficiency of milking systems (Sweeten and Wolfe, 1994), size of herd, and amount of rainfall-generated runoff from uncovered hard standings (Minogue et al., 2015). Dairy soiled water is collected separately from dairy slurry and the main disposal route is directly to land via landspreading or irrigation without any prior treatment. Because of its high volume and often unpredictable composition, DSW is frequently perceived to be of little or no agronomic benefit and is often applied repeatedly to land adjacent to the milking parlour (Wang et al., 2004). Storage of DSW is required at locations where landspreading is restricted due to adverse weather conditions, soil type, soil conditions, ground slope, proximity to water sources, and volumetric spreading limitations. In Ireland, for example, there is a legal requirement to provide a DSW storage capacity of 10 - 15 days (S.I. No. 31 of 2014), which results in increased infrastructure and associated costs for the dairy farmer. These costs, combined with the low nutrient replacement value of the DSW, mean that treatment and reuse may be a better option for the farmer.

The environmental impacts of repeated spreading of DSW on lands are well documented (e.g. Fenton et al., 2011), and may result in oxygen depletion and asphyxiation of aquatic life in surface waters, as well as a risk of nutrient leaching to groundwater (Knudsen et al., 2006). Long-term DSW application to lands may also result in soil accumulation of phosphorus (P) and heavy metals and increase concentrations of microbial pathogens, odorants and oestrogens in the receiving environment (Wang et al., 2004; Hao et al., 2008). Hence, there is a real need for cost-effective, low energy, and low maintenance on-farm treatment processes that would result in a reduced risk of pollution following application to land. Some multi-stage biological treatment processes, such as combined sequencing batch reactors (SBRs) and constructed wetlands (CWs) (Moir et al., 2005), and aerated settling tanks followed by vertical flow CWs (Merlin and Gaillot, 2010), have been used with varying degrees of success; however, much of the organic and nutrient reductions in these studies have been reported to occur in the aeration rather than in the passive processes. Passive treatment systems such as sand filters (Rodgers et al., 2005; Healy et al., 2007) and woodchip filters (Ruane et al., 2011; McCarthy et al., 2015) have also been investigated and have reported consistently high levels of organic, nutrient and pathogenic removal. Woodchip, in particular, is a cheap, biodegradable material which has potential use as a soil improver (Cogliastro et al., 2001; Miller and Seastedt, 2009) and has previously shown to be effective in improving effluent quality and ammonia emissions when used in out-wintering pads (Dumont et al., 2012).

In order to realise the full potential of woodchip filters, it is necessary to determine the optimum media depths which will produce consistently high quality effluent when subjected to variable strength influent DSW loading. Filters are usually designed and operated with one hydraulic regime selected to deliver an optimum organic loading rate (OLR). However, as the concentration of DSW varies seasonally (Rodgers et al., 2005), woodchip filters may be subjected to OLRs far in excess of their design capacity. Therefore, it is necessary to examine the performance of filters under these extreme conditions. Limited information is available on the impact of woodchip filter depths and OLRs on the quality of treated DSW effluent. Additionally, no information is available on the comparative performances of woodchip and sand filters when treating on-farm DSW.

As there are still knowledge gaps concerning the optimal design and operation of woodchip filters for the treatment of DSW, including the appropriate OLR and filter depth for optimal performance, the objectives of this study were to examine the impacts of filter depth and OLR on their performance when loaded with DSW and to compare them to sand filters operated under the same experimental conditions. An overarching objective of the study was to contribute to an improved understanding of the factors which should be considered in the design, construction and management of passive woodchip filters to treat on-farm DSW. Once such factors are resolved, pilot-scale filters may be effectively operated on the farm.

5.2 Materials and Methods

Eighteen filters, with internal diameters of 0.1 m and depths of either 0.6 m (*n*=3 columns) or 1 m (*n*=15 columns), were constructed using uPVC. All filters were open at the top and sealed at the base using uPVC end caps. The columns were placed on timber support frames and located in a temperature-controlled room at 10.6±0.7 °C and relative humidity of 86.9±4.5 % (replicating the average temperature and humidity in Ireland). A 0.075 m layer of clean, crushed pea gravel, manually sieved to a particle size of 10 – 14 mm, was placed at the base of each column to prevent washout of the filter media. Each column was then filled with either woodchip (with a particle size of 10 – 20 mm) or sand (effective size, d_{10} = 0.2, uniformity coefficient, UC = 1.4) by placing the selected media in 0.050 m lightly tamped increments. Influent DSW was pumped intermittently (four times per day, seven days per week) onto the filters using peristaltic pumps controlled by electronic timers. Hydraulic loading rates were adjusted using the manual flow control on the pumps and influent was distributed evenly across the surface of the filter media using perforated uPVC flow distribution plates (Fig. 5.1). Continuously operated submersible mixers were placed in each DSW influent container (one container per column set) to prevent stratification. Treated effluent samples from each filter were collected in an effluent collection container and all influent DSW samples were taken simultaneously from the influent containers.

To clean any organic material from the media, 70 L of potable water was pumped onto each filter over a period of 5 days prior to their operation, before being intermittently loaded with DSW for a period of 56 days. On day 15 of operation, each filter was seeded with 500 mL of nitrifying activated sludge (mixed liquor suspended solids, MLSS = 6,290 mg L^{-1}; sludge volume index, SVI = 143) collected from a local wastewater treatment plant. The period from day 0 to 56 was taken as the start-up period to reach steady state operation (defined by consistent chemical oxygen demand (COD), N and P effluent concentrations) for all filters and therefore day 56 was taken as the effective start day of the study (day 0).

This study compared three different operational setups to examine the impacts of (1) filter depth (2) OLR and (3) type of media (woodchip/sand) on filter performance. The filter configurations (Fig. 5.2) were (1) 0.6 and 1 m deep woodchip filters operating for 105 days with an average OLR of 120 g COD m^{-2} d^{-1} (2) 1 m deep woodchip filters operating for 105 days with average OLRs of 50 and 155 g COD m^{-2} d^{-1}, and (3) 1 m deep woodchip and sand filters operating for 220 days with an average OLR of 35 g COD m^{-2} d^{-1}. All configurations and treatments were constructed and operated at n=3. The very high OLRs (120 and 155 g COD m^{-2} d^{-1}) were selected to assess the performance of filters under extreme loading events, which may arise if a filter is designed and hydraulically loaded assuming a low influent organic concentration.

Dairy soiled water was collected weekly for the duration of the experiments in 25 L capacity containers from a dedicated DSW collection tank at a 150 cow dairy farm in south west Ireland (51°37'36"N 8°46'07"W). A submersible pump was used to fill the containers, which were then transferred directly to a temperature-controlled room (10.6±0.7 °C) in the laboratory. The average physical and chemical characteristics of the influent DSW are shown in Table 5.1.

Table 5.1 Physical and chemical properties of the influent DSW used in this study (n=3).

Parameter	Average ± standard deviation
COD (mg L^{-1})	2798±1503
SS (mg L^{-1})	874±614
TN (mg L^{-1})	81.5±34.1
NH_4-N (mg L^{-1})	63.9±32.3
TP (mg L^{-1})	29.8±14.4
DRP (mg L^{-1})	24.3±16.0
pH	7.22±0.71
Dry matter (%)	0.2±0.1

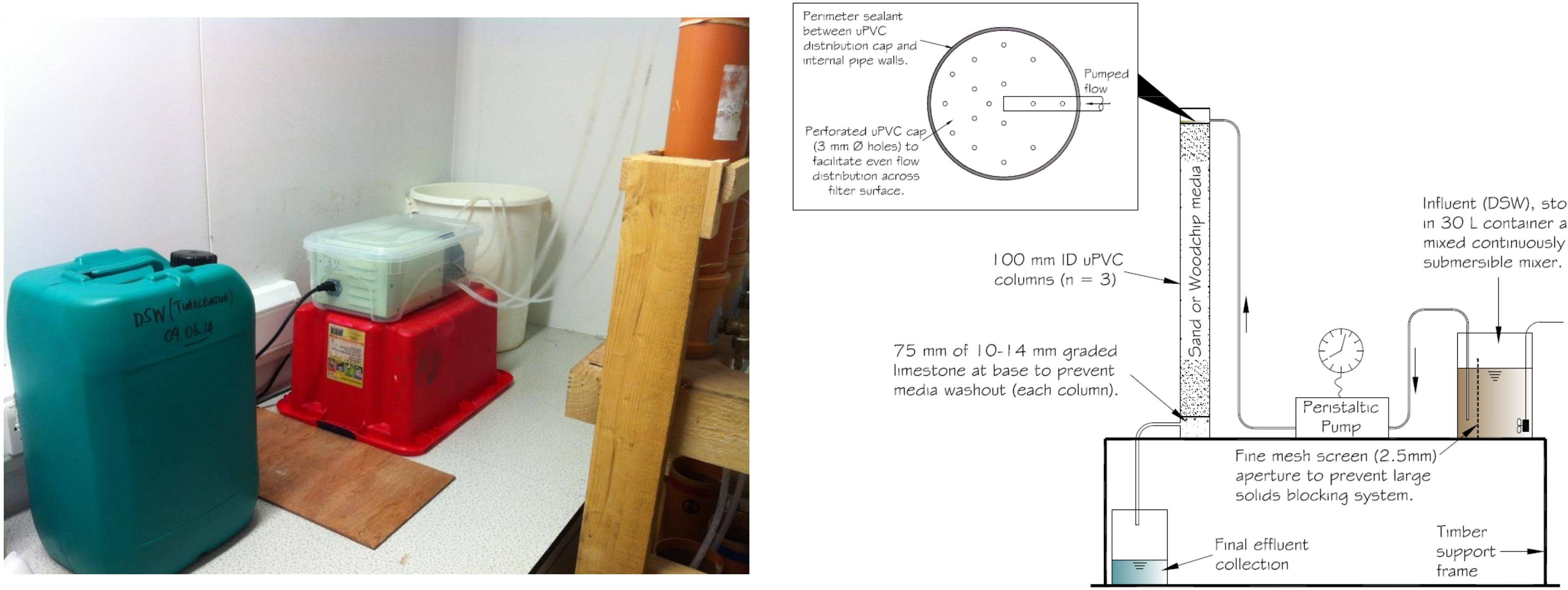

Figure 5.1 Laboratory filter setup and descriptive schematic. (Not to scale)

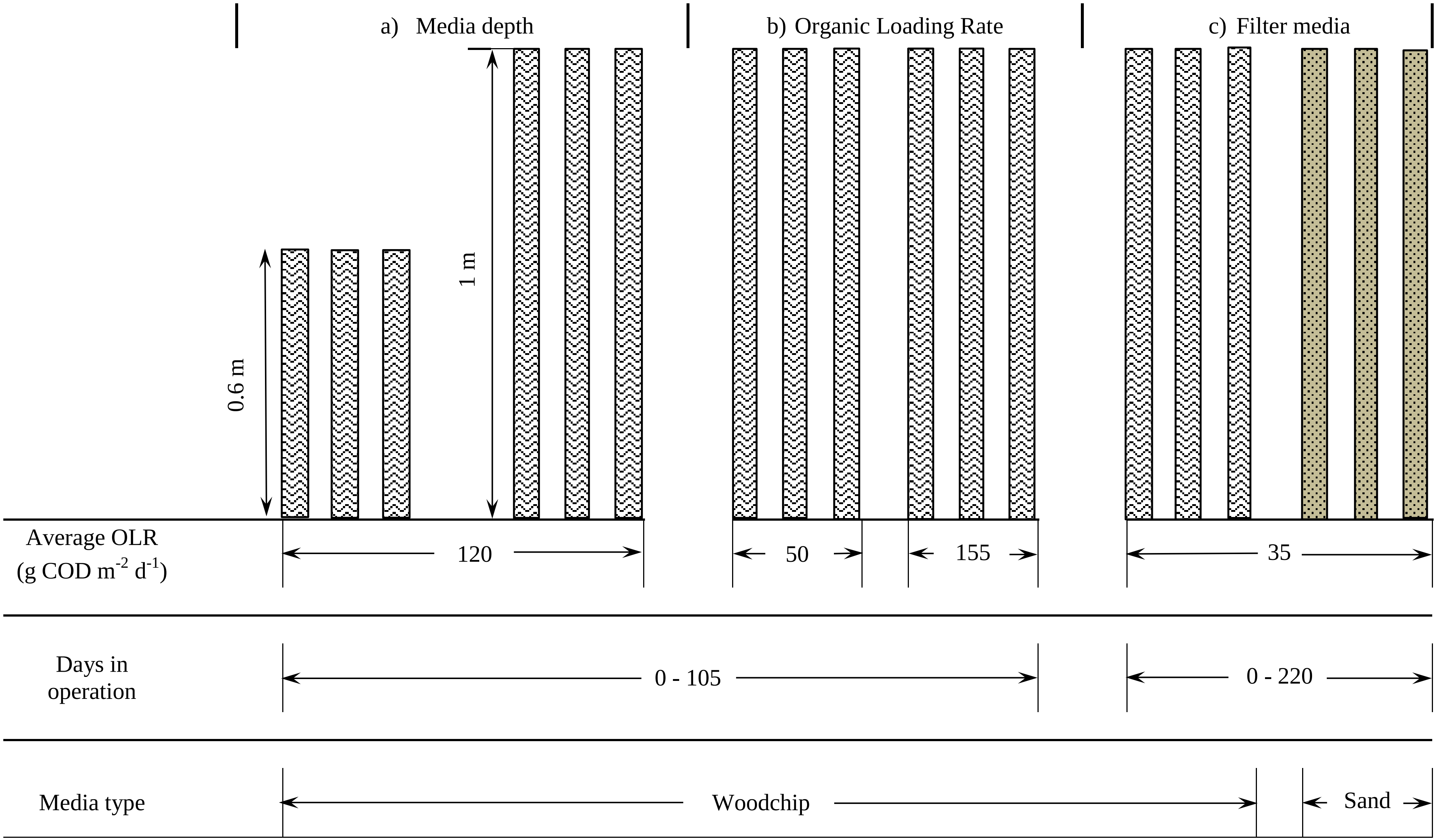

Figure 5.2 Combinations of a) media depth, b) organic loading rates and c) filter media used in this study. The woodchip used was 10 - 20 mm Sitka spruce (picea sitchensis). The sand used had a d_{10} = 0.2 mm and a uniformity coefficient (UC) = 1.4

The woodchip used was a commercial tree species, Sitca spruce (*Picea sitchensis*). Logs were debarked and then chipped using an industrial wood chipping machine (Morbark post peeler) at an industrial facility in northwest Ireland. The woodchips were sieved to a 10 – 20 mm grading prior to placing in the filter columns. The sand used was sourced from a commercial quarry in Co. Galway, West of Ireland and was graded to a d_{10} of 0.2 mm and a UC of 1.4. The permeability of the saturated woodchip and sand (Table 5.2) was measured using the constant head permeability test in accordance with BS 1377-5 (BSI, 1990).

The ability of the woodchip and sand media to remove N (measured as ammonium-N (NH_4-N)) and P (measured as dissolved reactive P (DRP)) from the DSW was investigated in a batch experiment by placing varying masses of the washed, graded media in flasks (*n*=3) and adding 40 mL of raw DSW to each sample. All samples were shaken for 24 h at 250 excursions per minute (epm) on a reciprocating shaker and on removal, were allowed to settle for 1 h, filtered through a 0.45 µm filter, and tested colorimetrically using a nutrient analyser (Konelab 20, Thermo Clinical Laboratories Systems, Finland). The data were then modelled using a Langmuir isotherm to establish maximum adsorption capacities (Table 5.2).

Table 5.2 Properties of the filter media used in this study (*n*=3).

Media Type	Grading	Hydraulic conductivity of saturated media (mm s^{-1})	Maximum adsorption capacity (mg kg^{-1})	
			P	N
Woodchip	10 – 20 mm	1.25	-	3
Sand	d_{10} = 0.2 mm; UC = 1.4	0.03	136	-

Influent samples and effluent taken from each filter column were tested for pH using a pH probe (WTW, Germany) and for suspended solids (SS) using vacuum filtration on a well-mixed subsample through Whatman GF/C (pore size 1.2 µm) filter paper. Sub-samples were filtered through 0.45 µm filters and analysed colorimetrically for DRP, NH_4-N, total oxidised N (TON) and nitrite-N (NO_2–N) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Nitrate-N was calculated by subtracting NO_2–N from TON. Unfiltered samples were tested for TP and filtered (0.45 μm) samples for total dissolved P (TDP) using acid persulphate digestion. Particulate P (PP) was calculated by subtracting TDP from TP. Unfiltered samples were tested for TN using a BioTector Analyzer (BioTector Analytical Systems Ltd., Cork, Ireland) and for COD (dichromate method). Influent DSW was tested for DM content by drying at 105 °C for 24 h. All water quality parameters were tested in accordance with standard methods (APHA, 2005).

5.2.1 Statistical analysis

The data were analysed using independent sample t-tests in SPSS (IBM SPSS Statistics 20 Core System) with column depth, OLRs and filter media as grouping variables. The data were checked for normality and, where necessary, were log transformed to satisfy the normal distributional assumptions required. Where normality was not achieved, the non-parametric Mann Whitney U test was used. Probability values of $p > 0.05$ were deemed not to be significant.

5.3 Results and Discussion

5.3.1 Impact of media depth

Treated effluent concentrations from the 1 m deep woodchip filters were consistently lower than those from the 0.6 m deep filters for all measured parameters at an OLR of 120 g COD m^{-2} d^{-1} (Fig. 5.3). However, the concentrations for COD in the final effluent (1469±587 mg L^{-1} for the 0.6 m filter and 587±113 mg L^{-1} for the 1 m filter) were still far in excess of the limit value for discharge to urban waters (125 mg L^{-1}; SI No 254 of 2001). The 0.6 m deep filters reduced COD, SS, TP and DRP by 46%, 54%, 7% and 5%, respectively (based on average influent and effluent concentrations), but did not reduce TN and NH_4-N concentrations to below those of the influent. Reductions of 78% COD, 95% SS, 85% TN, 82% NH_4-N, 50% TP and 54% DRP were measured for the 1 m deep filters and were consistent with those of Ruane et al. (2011), who measured reductions of 66% COD and 57% TN for 1 m deep woodchip filter pads operating at an average OLR of 173±43 g COD m^{-2} d^{-1} for a 1 year period. These findings indicate that filter depth is an important consideration in the design of woodchip filters, as the 0.6 m deep filters did not provide sufficient detention time to reduce COD and SS by more than approximately 50% at an average OLR of 120 g COD m^{-2} d^{-1}. These removals were increased by a factor of approximately 1.7 when the filter depth was increased to 1 m with consequent increase in detention time.

Ammonium-N was not nitrified in any of the woodchip filters and this was most likely as a result of the high average C:N ratio (30) of the influent DSW, which was far above the optimum C:N ratio of 3 - 6 for nitrification (Henze et al., 2001; Eding et al., 2006). This, combined with a high OLR (120 g COD m^{-2} d^{-1}), likely resulted in the formation of a dense, non-porous heterotrophic biofilm structure, reducing the available sites for the slow growing nitrifiers (Okabe et al., 1996; Wijeyekoon et al., 2004; Nogueira et al., 2002). A nitrogen mass balance between influent and effluent carried out on the 0.6 m deep filters showed that the mass of organic nitrogen (Norg) was reduced by 23% while the mass of NH_4-N increased by 8%, with no overall TN removal. For the 1 m deep filters, the mass of N_{org} was reduced by 37% with a corresponding reduction in NH_4-N of 82% and an overall decrease in TN of 85%, with NH_4-N as the dominant fraction in the final effluent. Therefore, while significant TN and NH_4-N removals were achieved in the 1 m deep filters (85% and 82%, respectively), the removal processes were by physical filtration of SS and associated N (Fig. 5.4(A)) rather than biological transformations. Much lower SS removals were measured in the 0.6 m deep filters (Fig. 5.3). The average pH of the treated effluent was 7.41±0.26 and alkalinity 273.7±8.5 mg $CaCO_3$ L^{-1}, indicating that alkalinity was not an inhibiting factor for nitrification. Ruane et al. (2011) reported an average concentration of 22.5 mg NO_3-N L^{-1} in treated effluent from 1 m deep woodchip filter pads loaded with DSW, which had an average influent concentration of 12.9 mg NO_3-N L^{-1} and C:N ratio of 16. In the current study, there was no NO_3-N in the influent and this may have influenced the biofilm formation and consequent opportunity for development of NH_4-N oxidizers (Okabe et al., 1996).

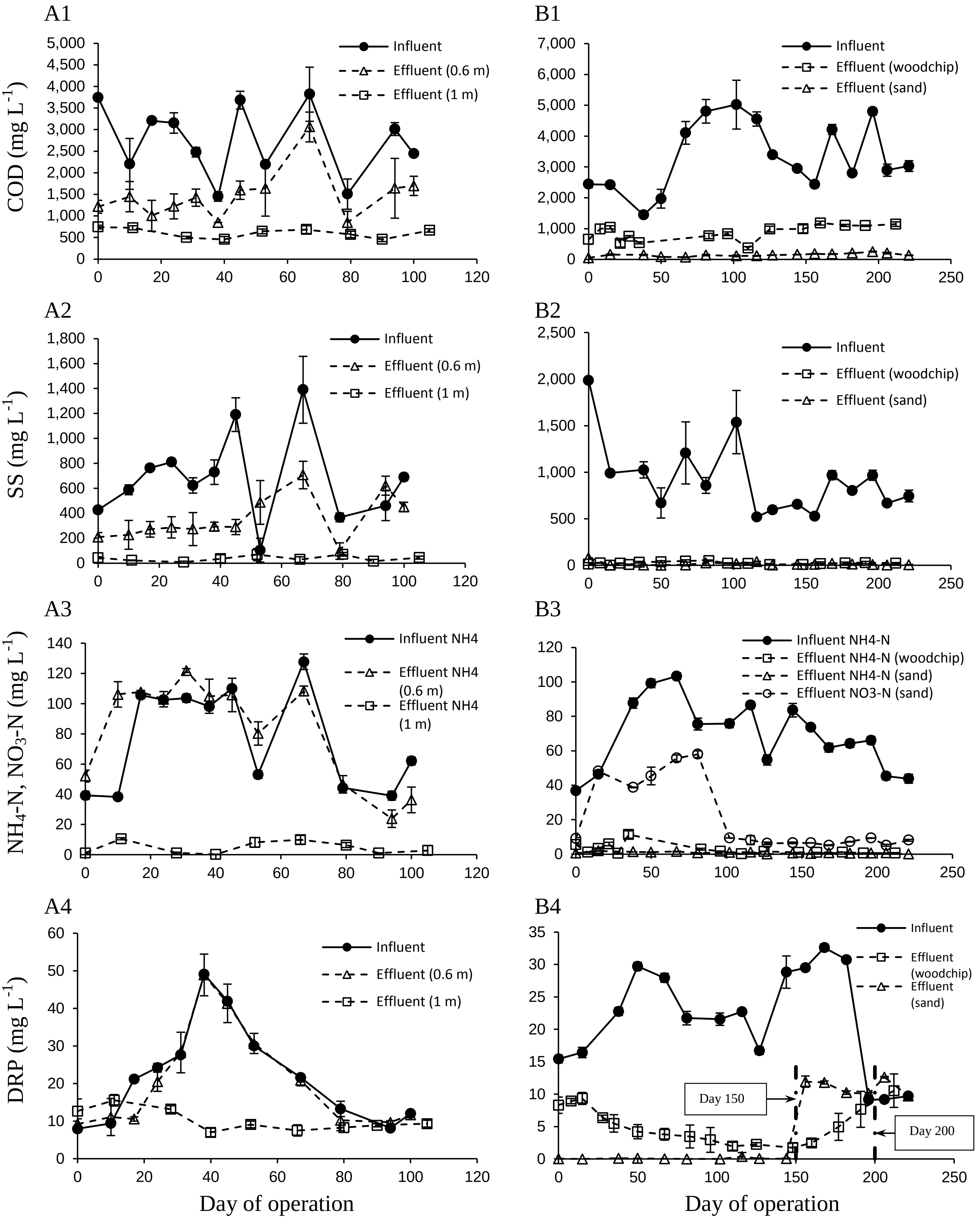

Figure 5.3 Impact of media depth (A1 – A4) and media type (B1 – B4) on COD, SS, NH_4-N and DRP removals. An average organic loading rate of 120 g COD m^{-2} d^{-1} was applied to woodchip media (10 – 20 mm Sitka spruce) when comparing the impact of media depth (A1 – A4). An average organic loading rate of 35 g COD m^{-2} d^{-1} was applied to woodchip (10 – 20 mm Sitka spruce) and sand (d_{10} = 0.2 mm, UC = 1.4) media, both 1 m deep when comparing the impact of media type (B1 - B4). Error bars indicate standard deviations.

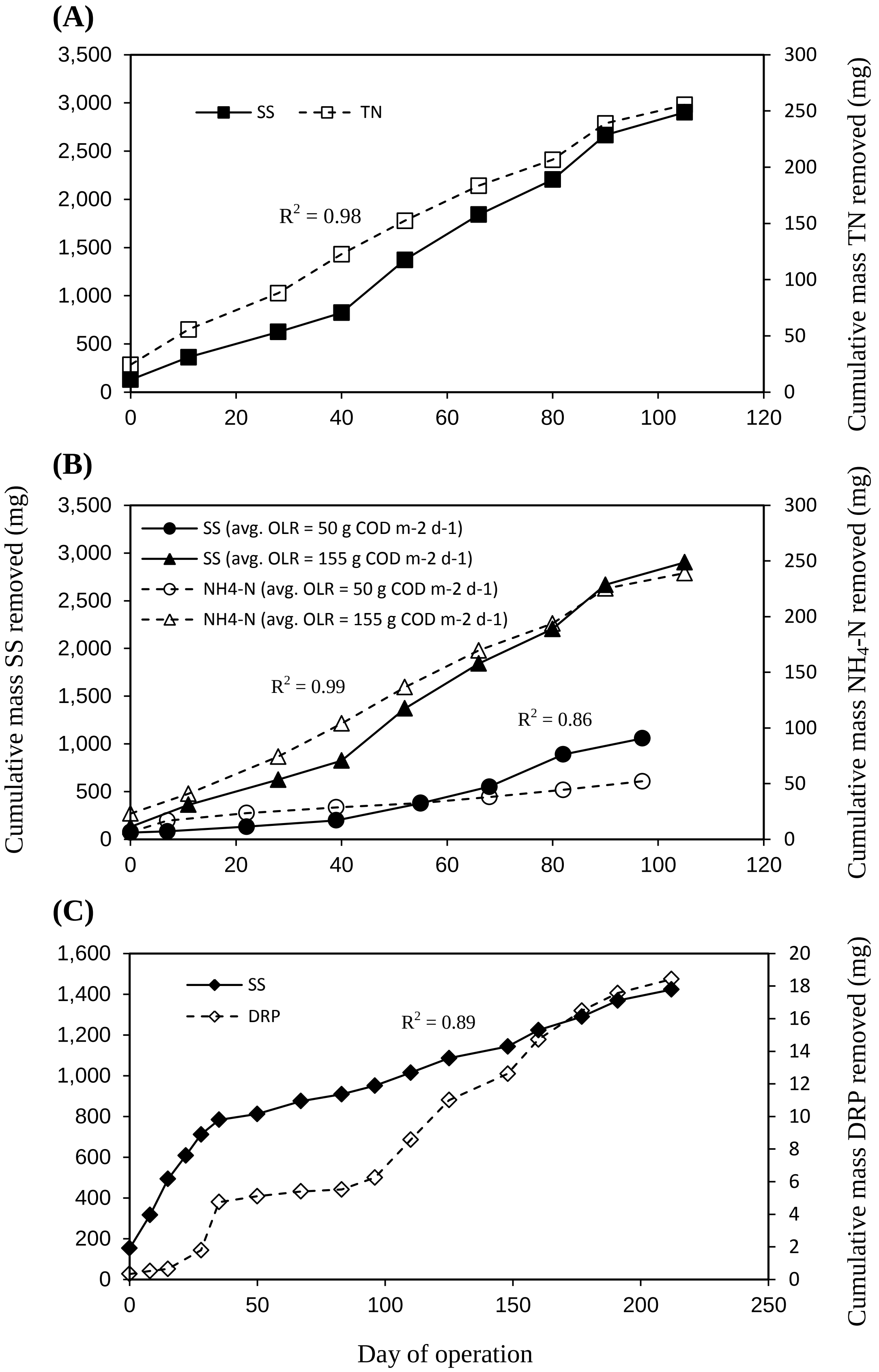

Figure 5.4 Correlations between cumulative mass removals of suspended solids (SS) for 1 m deep × 0.1 m Ø woodchip filters (*n*=3, each set) and **(A)** TN loaded at 120 g COD m^{-2} d^{-1} **(B)** NH$_4$-N loaded at 50 and 155 g COD m^{-2} d^{-1} respectively and **(C)** DRP loaded at 35 g COD m^{-2} d^{-1}. Correlation coefficients, (R^2) indicated.

5.3.2 Impact of organic loading rates

There were no significant differences in the final effluent concentrations of NH_4-N (4.1±4.1; 4.6±4.2 mg L^{-1}) and SS (23±16; 37±22 mg L^{-1}) from the 1 m deep woodchip filters operated at OLRs of 50 and 155 g COD m^{-2} d^{-1}; however, the average effluent DRP concentration (3.8±1.5 mg L^{-1}) from the 50 g COD m^{-2} d^{-1} filters was significantly lower ($p<0.001$) than from the 155 g COD m^{-2} d^{-1} filters (10.2±2.9 mg L^{-1}). As the woodchip had no ability to adsorb P (Table 5.2), physical removal was the main mechanism for P removal. Based on the influent and effluent loading rates, 2.5 mg PP d^{-1} (318 mg PP m^{-3} d^{-1}) was retained in the 155 g COD m^{-2} d^{-1} filters, whereas 0.4 mg PP d^{-1} (51 mg PP m^{-3} d^{-1}) was retained in the 50 g COD m^{-2} d^{-1} filters.

Removals (based on the average influent and effluent load and expressed in mg d^{-1}) in the range of 71% to 97% were measured for COD, SS, TN and NH_4-N, and 54% to 74% for TP and DRP, were measured in both sets of filters. Final effluent concentrations of SS, NH_4-N and DRP ranged from 23 to 37 mg L^{-1}, 4.1 to 4.6 mg L^{-1}, and 3.8 to 10.4 mg L^{-1}, respectively. However, the final effluent COD concentrations from both filters (766±221 mg L^{-1} for the 50 g COD m^{-2} d^{-1} filters and 604±112 mg L^{-1} for the 155 g COD m^{-2} d^{-1} filters) were well above the limit values for discharge to urban waters in Ireland (S.I. No 254 of 2001). Effluent mass loads for COD, SS, NH_4-N and DRP (Fig. 5.5) remained consistent over the duration of the study period, highlighting the capacity of the filters to effectively and consistently treat variable strength and variably loaded influent DSW.

Negligible NO_3-N concentrations were measured in the effluent, underlining the reliance on physical filtration for NH_4-N removal as illustrated by the close correlations between SS and NH_4-N mass removals for both loading rates (Fig 5.4(B)).

5.3.3 Impact of filter media

There were no significant differences between the treated effluent from 1 m deep woodchip and 1 m deep sand media (average OLR = 35 g COD m^{-2} d^{-1}) for SS (23±13 and 16±20 mg L^{-1}) and NH_4-N (2.9±3.4 and 0.8±0.5 mg L^{-1}); however, the sand outperformed the woodchip in COD removal (a final effluent of 146±52 mg L^{-1}

versus 873±242 mg L^{-1}) and DRP removal up to day 150 (a final effluent of 0.1±0.1 mg DRP L^{-1} versus 4.9±2.7 mg DRP L^{-1}). The enhanced COD removals in the sand filters were reflective of their higher hydraulic retention time when compared to the woodchip filters (the hydraulic conductivity of the sand was >40 times lower than that of the woodchip (Table 5.2)). The enhanced DRP removals in the sand filters were as a result of their higher P adsorption capacity (136 g DRP kg^{-1}) compared with the woodchip, which had no affinity for P, and DRP reductions in the woodchip filters were associated with SS removals (Fig. 5.4(C)). After 150 days of operation, DRP breakthrough occurred quite quickly in the sand filters and at a slower rate in the woodchip filters (Fig. 5.3). From day 200 to the end of the study, neither the sand nor the woodchip filters removed any DRP from the influent DSW (Fig. 5.3). The average mass of P retained up to day 150 was 1.61±1.30 and 3.89±0.76 mg TP d^{-1}, 0.61±0.31 and 0.96±0.32 mg PP d^{-1} and 1.33±0.84 and 2.58±0.60 mg DRP d^{-1} for woodchip and sand filters, respectively, indicating that the sand was more effective at removing PP and also had a greater affinity for adsorption of DRP (Table 5.2). The mass removal rates also indicate that sand had more consistent P removal than woodchip up to day 150.

During the first 85 days of operation, nitrification occurred in the sand filters and the NO_3-N concentration rose from 0.1±0.1 mg L^{-1} in the influent to 43±18 mg L^{-1} in the effluent. However, the effluent NO_3-N subsequently reduced considerably, and attained an average concentration of 7.2±1.6 mg L^{-1} by the end of the study (Fig. 5.3). The reasons for the suppressed levels of NO_3-N were possibly due to the preferential formation of heterotrophic-dominated biofilm layers limiting dissolved oxygen (DO) to the nitrifiers (Nogueira et al., 2002) as a consequence of the high influent C:N ratios in the influent wastewater (average of 38). Negligible NO_3-N concentrations were measured in the treated effluent from the woodchip filters and were always below 0.21±0.19 mg L^{-1}. This indicates that even at the low OLRs used in this study, which are at the upper limit at which nitrification normally occurs in sand filters treating a similar type of wastewater (around 30 g COD m^{-2} d^{-1}; Rodgers et al., 2005), woodchip filters are unable to nitrify DSW.

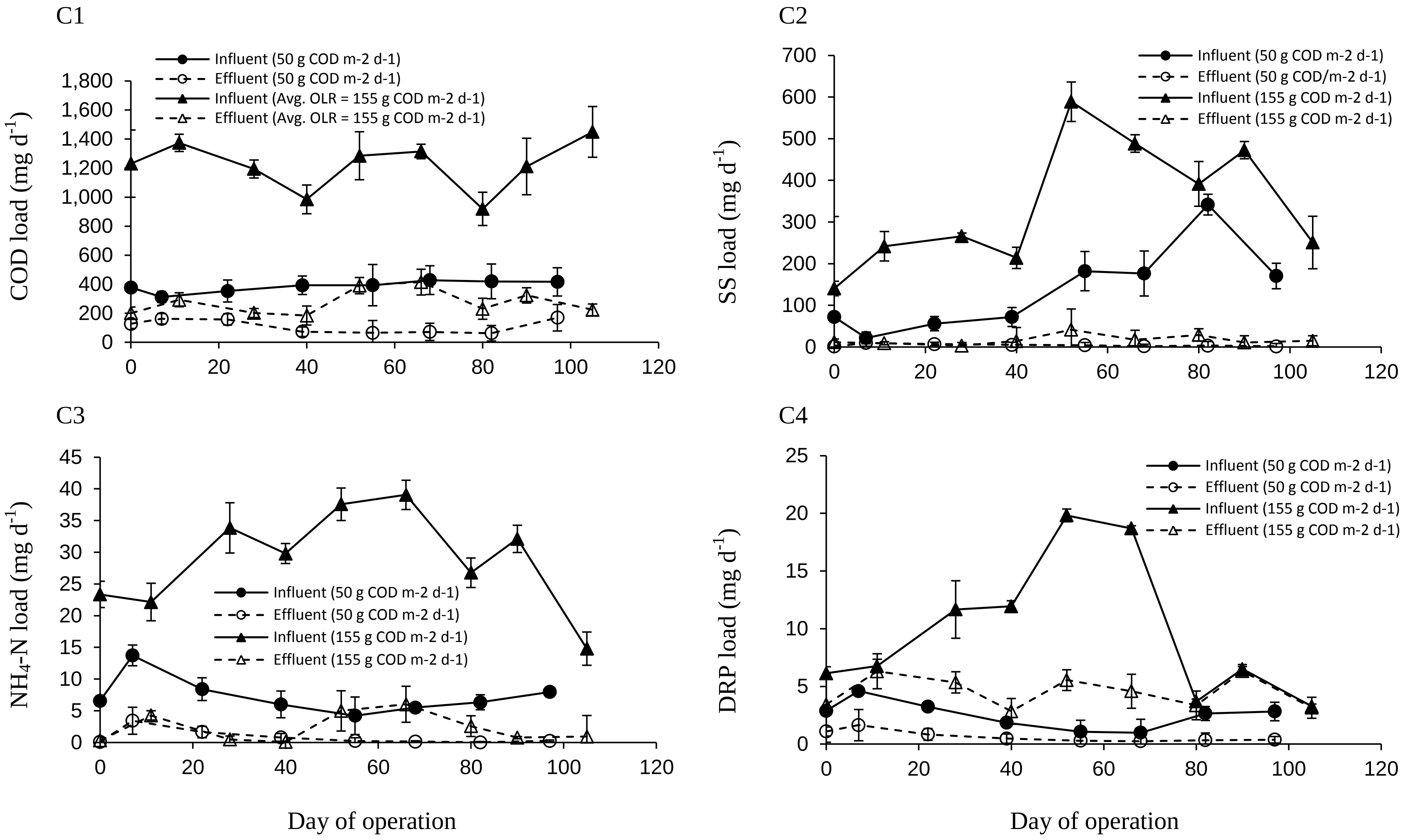

Figure 5.5 Impact of organic loading rates on chemical oxygen demand (COD), suspended solids (SS), ammonium (NH$_4$-N) and dissolved reactive P (DRP) mass removals. The filter material used was 10 – 20 mm Sitka spruce woodchip, 1 m deep. Error bars indicate SD

5.3.4 Assessment of optimum filter media, configuration and operation

When assessing the suitability of the filters to treat on-farm DSW, key operating criteria must be taken into account, together with the main objective of reducing organic and nutrient concentrations to levels which would not adversely impact the environment if landspread. These operating criteria include items such as cost and availability of the media, robustness and longevity of performance (i.e. how well can media deal with daily and seasonal variations in flow and strength and for how long), biodegradability, and disposal of spent media.

The results of this study show that woodchip filters should have a minimum depth of 1 m to achieve required removals and can reduce the measured water quality parameters at OLRs up to at least 155 g COD m^{-2} d^{-1}. However, based on the N mass balances and effluent concentrations of NO_3-N measured in this study, the removal mechanisms in woodchip filters are primarily physical (straining) and not biological (nitrification did not occur). The suppression of biological activity may have been a function of the OLRs employed in this study, where the lowest OLR studied (35 g COD m^{-2} d^{-1}) was still at the upper limit at which nitrification normally occurs in filters (Rodgers et al., 2005).

Biological N transformations are a sustainable long-term process to reduce effluent N when compared to removal by physical straining alone. While nitrification was not observed to occur in the woodchip filters in the current study, other studies (e.g. Carney et al., 2011) have reported its occurrence for piggery wastewaters at OLRs in the range 14 - 128 g COD m^{-2} d^{-1}. Nitrification of DSW in sand filters has been reported in many studies (e.g. Rodgers et al., 2005; Healy et al., 2011) at OLRs in the range 20 – 40 g COD m^{-2} d^{-1}. Given that the composition of raw DSW normally contains very low, if any, NO_2 or NO_3 concentrations (Minogue et al, 2015), long start-up times are likely to be required to establish an active population of NH_4 oxidizers in any filter medium (Okabe et al, 1996; Lekang and Kleppe, 2000).

Surface clogging of the filter media is an operational issue that must be considered for on-farm use and while neither the sand nor the woodchip media in this study experienced surface clogging, Healy et al. (2007) reported clogging of sand filters after 42 days at an OLR of 43 g COD m^{-2} d^{-1}. In contrast, we are not aware of any reported issues with surface clogging of woodchip media, and it has been estimated that a woodchip filter may be operational for 2 – 3 years before surface ponding occurs (Ruane et al., 2011).

The decision to use woodchip or sand filter media is ultimately taken by synthesizing environmental benefits versus capital and operating costs. Operating costs are similar for both woodchip and sand filters (the modes of operation are identical for both), while capital costs are differentiated only by the cost of the media (filter setup for woodchip and sand are similar), which may also not differ significantly and will be location specific. Cost comparisons therefore can be made by comparing the required footprint of woodchip and sand media, both at a depth of 1 m – the minimum acceptable filter depth identified in this study. Based on the optimal OLRs identified in this study (an OLR of 155 g COD m^{-2} d^{-1} for woodchip filters, which treated the wastewater through physical processes, if not necessarily biological processes, and an OLR of 35 g COD m^{-2} d^{-1} for sand filters, which only temporarily caused the occurrence of nitrification, but clearly was at the upper OLR limit at which such filters may be operated), a filter surface area of 0.48 m^2 cow^{-1} for woodchip versus 2.1 m^2 cow^{-1} for sand would be required (Table 5.3). The larger area required for the sand filter combined with their lack of robustness to deal with shock loads (Healy et al., 2007) and the potential for surface clogging (Rodgers et al., 2005), indicate that woodchip filters are a better on-farm treatment option.

Table 5.3 Comparative filter areas (per cow) of a full scale filter for average organic loading rates investigated in this study of 155 g COD m^{-2} d^{-1} for woodchip and 35 g COD m^{-2} d^{-1} for sand.

Q^1	COD load^2	Filter area per cow (m^2)	
(L d^{-1} cow^{-1})	(g COD d^{-1})	Woodchip^3	Sand^4
27	73.7	0.48	2.1

[1] Minogue et al., 2015;
[2] Assuming an annual average COD concentration of 2,750 mg L^{-1};
[3] Using an OLR of 155 g COD m^{-2} d^{-1};
[4] Using an OLR of 35 g COD m^{-2} d^{-1}.

The optimal filter configuration identified in the current study produced a final effluent that was in excess of permissible discharge standards. For the water to be discharged to surface waters, some form of primary and tertiary treatment may be required. Primary treatment may consist of a simple sedimentation tank upstream of the woodchip filters to reduce SS in the influent DSW, and tertiary treatment might comprise the addition of downstream polishing filters using, for example, zeolite for enhanced N removal and flue gas desulphurization (FGD) gypsum for enhanced P removal. However, this would be costly for the farmer and, moreover, would mean that a discharge license may be required. Additionally, the technical and economic feasibility of using such tertiary media to act as polishing filters for DSW treatment would need to be established. Based on the results of the current study, a 1 m deep woodchip filter, with an OLR of 155 g COD m^{-2} d^{-1}, may retain up 600 mg SS d^{-1} (Fig. 5.5) and may reduce over 90% of the SS. Therefore, the liquid portion of the wastewater may be used in irrigation, which requires no discharge license or transport costs, and is safer (Augustenborg et al., 2008a); and, once exhausted, the spent timber residue may be incorporated into the soil (Augustenborg et al., 2008b).

5.4 Conclusions

On the basis of this study, woodchip filters are more effective in the treatment of DSW than sand filters. In this study, optimal performance in terms of mass of contaminants removed per day was achieved using a 1 m deep woodchip filter operated at an OLR of 155 g COD m^{-2} d^{-1}. Filtration was the dominant mechanism for N removal in the woodchip filters. The final effluent was above the concentrations at which it may be legally discharged to receiving waters. Therefore, management option employed to re-use the final effluent may be to use the liquid portion of the effluent in irrigation and, in time, to incorporate the spent timber residue into the soil.

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Chapter 6 – Conclusions and Recommendations

6.1 Overview and context

The first hypothesis of this study was that combined application of chemical and zeolite amendments with agricultural wastes would reduce nitrogen (N), phosphorus (P), carbon (C) and suspended solids (SS) losses in surface runoff from land applied dairy and pig slurries, and dairy soiled water (DSW) under simulated rainfall. The realisation of this hypothesis was demonstrated in the first two studies (**Chapters 2 and 3**). The key findings of **Chapter 2** were that the combined amendments were particularly effective in reducing N, P and SS losses from dairy slurry (range 70 – 87%) and pig slurry (range 47 – 92%), and less effective for DSW (25 – 50%). Their effectiveness to reduce runoff losses was correlated with their ability to prevent SS being washed off the surface by the rainfall and was reduced with decreasing dry matter (DM) content of the agricultural wastes. The key findings of **Chapter 3** were that while the combined amendments reduced total organic C (TOC) losses from dairy (76%) and pig (65%) slurries, and DSW (51%), the relatively low amounts of TOC measured in runoff from unamended slurries when compared with the amounts applied (2, 3 and 17% for dairy and pig slurries and DSW, respectively) meant that the use of amendments to mitigate C losses in runoff may not be economically viable.

While these results are significant, it is important to view them in the context of a field study. The rainfall simulation experiment assessed N, P, C and SS losses in runoff from an isolated 0.225 m^2 area of soil with a relatively steep slope (10%), relatively intense and persistent simulated rainfall (9.6 mm h^{-1} for 30 mins), and with no capacity to drain water vertically to reduce saturation excess runoff. In a field study, the rainfall would typically be less intense and persistent, the slope might be more or less than that used for this study, and the soil would have some capacity for vertical drainage. Therefore, the rainfall runoff experiment represented a worst case scenario in terms of potential N, P, C and SS losses from the soil. Additionally, in small scale experiments such as the rainfall simulation study, the attenuation of contaminants during transport is limited due to the small soil surface area being used.

Therefore, while losses from the runoff boxes may be used to assess the relative merits of the amendments and the effect of time intervals between rainfall events, they may not accurately represent the quantitative contaminant losses to surface water bodies that might be expected in the landscape.

A follow-on study to investigate the effectiveness of the combined amendments to also reduce leaching losses of N, P and C and greenhouse gas (GHG) emissions of carbon dioxide (CO_2) and methane (CH_4) from surface applied dairy and pig slurries, and DSW using packed soil columns is included in **Chapter 4**. This study yielded disappointing results, which did not realise the second hypothesis of this thesis and concluded that in the short term at least, the amendments did not mitigate the risks of N, P and C leaching or GHG emissions of CO_2 and CH_4 from the surface applied wastes. The study also found that pig slurry, whether amended or unamended, posed the greatest short term environmental threat of leaching and CO_2/CH_4 emissions.

It is worth noting that in this experiment leaching losses were measured from repacked soil columns, where the soil structure was disturbed during the repacking process and which had bare surfaces with no crop growth. Consequently, this would represent a worst case scenario for leaching losses of N, C and dissolved P, but not necessarily for particulate P, which typically migrates through macropores in undisturbed soil. The use of distilled water to irrigate the columns may also have impacted the extent of leaching as rainwater, which contains solutes and ions typically has a higher electrical conductivity than distilled water. Notwithstanding these imperfections, however, the use of repacked soil columns to evaluate the relative impacts of the applied amendments is appropriate, if not completely reflective of quantitative losses in field conditions.

Nitrogen losses via ammonia (NH_3) and nitrous oxide (N_2O) emissions are an important consideration for land applied agricultural wastes. Nitrous oxide is a potent GHG, while high levels of NH_3 in the atmosphere of concentrated animal rearing facilities are known to adversely impact the health and productivity of the animals as well as the health of workers in these facilities, for example poultry rearing facilities. The use of alum to mitigate NH_3 losses from poultry manure has long been regarded as a cost effective best management practice in the USA and has the added benefit of reducing pathogens in poultry litter. The use of amendments to also reduce NH_3 and potentially N_2O emissions in other types of concentrated animal feeding organisations (CAFOs) are likely to gain importance if this type of operation continues to become more prevalent. Measurement of these gases from future agricultural waste treatment experiments should therefore be prioritised.

The treatment of DSW is an important issue for farmers, as it directly impacts their animal waste storage requirements and needs to be regularly disposed of throughout the year. Reuse of DSW as a washwater is also likely to gain importance in the context of a global push for water conservation and reuse. The third hypothesis of this study was that woodchip is a better medium than sand to passively treat DSW and the laboratory study detailed in **Chapter 5** supports that hypothesis. Management of the filters is considered to be one of the key issues with upscaling to on-farm DSW treatment. For example, when the woodchip media becomes exhausted, it rapidly becomes a source rather than a sink for pollutants, and so timely replacement of the media is critical to the proper functioning of the filters. In addition, there are legislative issues that need to be overcome, such as obtaining a wastewater discharge licence, which requires regular effluent sampling, analysis and reporting to the licencing authority.

6.2 Conclusions

The main conclusions of this study are:

- Combined use of zeolite and chemical amendments, when mixed with dairy and pig slurries and DSW, reduced losses of N, P and SS in surface runoff to a much greater extent than those from unamended slurries. However, the combined amendments were most effective when mixed with dairy slurry, followed by pig slurry, and were least effective when used with DSW. The impact of the amendments was correlated with the DM of the slurries and the relative effectiveness of the amendments to flocculate P, N and SS-enriched slurry particles. The findings of this study are reported in **Chapter 2** (Paper 1).

- Combined use of zeolite and chemical amendments when mixed with dairy and pig slurries and DSW, reduced total organic C (TOC) losses in surface runoff. The largest reduction was for dairy slurry, followed by pig slurry, and the smallest reduction was for DSW. While effective, the combined use of zeolite and chemical amendments may not be economically viable for use with organic slurries to reduce C losses, given the relatively low amounts of TOC measured in runoff from unamended slurries compared with the amounts applied. The findings of this study are reported in **Chapter 3** (Paper 2).

- Combined use of zeolite and chemical amendments when mixed with pig slurry and DSW did not reduce leaching losses of N, P and C, or gaseous emissions of CO_2 and CH_4, when compared to unamended slurries. While use of the combined amendments mixed with dairy slurry reduced leaching losses of C, they also increased CO_2 emissions. The greatest short term threat of nutrient leaching and gaseous emissions of CO_2 and CH_4 was posed by pig slurry, both amended and unamended. The findings of this study are reported in **Chapter 4**.

- Woodchip filters were effective in treating intermittently loaded DSW up to a maximum OLR of 155 g chemical oxygen demand (COD) m^{-2} d^{-1}. Reductions of 78% COD, 95% SS, 85% total N, 82% ammonium-N (NH_4-N), 50% total P, and 54% dissolved reactive P were measured using 1 m deep woodchip filters, and were greater than corresponding reductions for 0.6 m deep woodchip filters.

- Woodchip filters up to 1 m deep did not nitrify the DSW even at relatively low loading rates (35 g COD m^{-2} d^{-1}) due mainly to inadequate hydraulic retention times (HRTs). The primary removal mechanism for all contaminants using woodchip filters was physical (i.e. straining) as opposed to biological. When operated at the same OLR and when of the same depth, sand filters had better COD removals (96%) than woodchip (74%), but there was no significant difference between them in the removal of SS and NH_4-N.

The sand filters nitrified the effluent (43±18 mg NO_3-N L^{-1}) for the first 85 days of operation, but thereafter concentrations reduced to 7.2±1.6 mg NO_3-N L^{-1}.

- Woodchip filters were assessed to be more economically and environmentally effective in treating DSW than sand filters. Optimal performance for woodchip filters may be achieved using a minimum depth of 1 m, operated at a maximum OLR of *c.* 155 g COD m^{-2} d^{-1}. The likelihood of clogging makes sand filters less desirable than woodchip filters. The final filtered effluent from both sand and woodchip filters was above the concentrations at which it may be legally discharged to receiving waters. Therefore, possible reuse options may be to use the treated effluent for irrigation and, in time, to incorporate the spent timber residue into the soil. The findings of this study are reported in **Chapter 5** (Paper 3).

6.3 Recommendations

This study was carried out using laboratory-based experiments and represents a critical first step to assess the effectiveness of combined amendments to mitigate nutrient losses and gaseous emissions from land applied dairy and pig slurries, and DSW. The laboratory-based filter study to examine the impacts of filter depth, OLRs, and media type on their effectiveness to treat DSW, was also an important assessment prior to establishing field and catchment-scale studies. Although a farm-scale filter unit to treat DSW was constructed and operated (**Chapter 1**), there were no long term results established and the experiment was aborted because of its failure to nitrify the effluent. Therefore, there is a need to establish long term testing in field situations which may highlight management requirements that may not be obvious in the laboratory, such as clogging and surface sealing of filters over time, the practicalities of co-mixing amendments with slurries prior to landspreading, and the long term effects of applying chemical amendments to soil. Consequently, the following non exhaustive list of recommendations applies this study:

- A long term plot study to evaluate the effectiveness of zeolite and chemical amendments mixed with dairy slurry in particular, to mitigate surface runoff losses should be carried out. This study should include repeated seasonal slurry applications and measure its impact on soil structure and chemistry over the duration of the study. This study should also examine soil leaching losses and GHG emissions of CO_2, CH_4 and N_2O;

- There is a need to focus on sustainable long term solutions to prevent or at least reduce nutrient leaching from pig slurry, particularly where it is spread repeatedly in concentrated areas. Application of combined zeolite and PAC did not reduce leaching losses of N, P and C from a single application, and it is thought that repeated slurry applications may lead to even higher nutrient losses than from a single application;

- Prior to their use, a life cycle assessment of the amendments used in this study should be conducted to ensure that their application is environmentally sustainable and economically viable;

- The failure of woodchip filters to nitrify was a main weakness in their treatment of on-farm DSW. Options to examine ways in which this can be achieved without compromising the ability of the filters to withstand surface clogging, while simultaneously maintaining sufficient aeration throughout the filter bed, need to be examined. This remains a challenge and one possibility might be the use of dual media filters or a design which would lengthen the flow path (and consequently the HRT) within the aerobic filter;

- Treatment of filtered DSW to a standard suitable for reuse as washwater should be explored. In this study, the treated DSW was in excess of permissible discharge standards and, if required to be discharged or reused as washwater, additional treatment will be required. This might be achieved by provision of downstream polishing filters, but would also require some form of on-site disinfection facilities, if required to be used within a milking parlour area.

Appendix A

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WASTE MANAGEMENT

Use of Zeolite with Alum and Polyaluminum Chloride Amendments to Mitigate Runoff Losses of Phosphorus, Nitrogen, and Suspended Solids from Agricultural Wastes Applied to Grassed Soils

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

Abstract

Diffuse pollutant losses containing phosphorus (P), nitrogen (N), and suspended solids (SS) can occur when agricultural wastes are applied to soil. This study aimed to mitigate P, N, and SS losses in runoff from grassed soils, onto which three types of agricultural wastes (dairy slurry, pig slurry, and dairy-soiled water [DSW]), were applied by combining amendments of either zeolite and polyaluminum chloride (PAC) with dairy and pig slurries or zeolite and alum with DSW. Four treatments were investigated in rainfall simulation studies: (i) control soil, (ii) agricultural wastes, (iii) dairy and pig slurries amended with PAC and DSW amended with alum, and (iv) dairy and pig slurries amended with zeolite and PAC and DSW amended with zeolite and alum. Our data showed that combined amendments of zeolite and PAC applied to dairy and pig slurries reduced total P (TP) in runoff by 87 and 81%, respectively, compared with unamended slurries. A combined amendment of zeolite and alum applied to DSW reduced TP in runoff by 50% compared with unamended DSW. The corresponding reductions in total N (TN) were 56% for dairy slurry and 45% for both pig slurry and DSW. Use of combined amendments reduced SS in runoff by 73 and 44% for dairy and pig slurries and 25% for DSW compared with unamended controls, but these results were not significantly different from those using chemical amendments only. The findings of this study are that combined amendments of zeolite and either PAC or alum reduce TP and TN losses in runoff to a greater extent than the use of single PAC or alum amendments and are most effective when used with dairy slurry and pig slurry but less effective when used with DSW.

Core Ideas

- Surface runoff studies have mainly focused on mitigation of one contaminant.
- This paper optimizes mitigation of two contaminants by optimizing amendments.
- Zeolite and chemical mixtures increased N and P removal from agricultural waste.
- More N and P were removed from zeolite and chemical mixtures than chemicals only.
- Zeolite and chemical mixtures improved suspended solids removal from dairy soiled water runoff.

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Excessive application of agricultural waste to soils may have environmental impacts, including phosphorus (P), nitrogen (N), and suspended solids (SS) losses and increased greenhouse gas emissions (Smith et al., 2001a; Chadwick et al., 2011; Kröger et al., 2013; McDowell and Hamilton, 2013). Loss of P, N, and SS in overland flow is affected by the time interval between surface application and rainfall events (Allen and Mallarino, 2008; Hanrahan et al., 2009), antecedent hydrologic conditions (Brennan et al., 2012), flow path length (McDowell and Sharpley, 2002), surface slope (Alaoui et al., 2011), soil type (Wall et al., 2013), and the short-term and long-term effects of agricultural waste application to the soil structure (McDowell et al., 2004). Event P losses in surface runoff after land application of agricultural wastes may be dominated by particulate P (PP) (Preedy et al., 2001) or by dissolved P, depending on individual circumstances, such as grazing animals, type of stock, topography, and degree of exposure of the soil to rainfall events (Hart et al., 2004), whereas most of the permanent P losses in surface runoff from soils are in dissolved form (Heathwaite and Dils, 2000). Nitrogen losses are dominated by ammonium (NH_4–N) (Heathwaite et al., 1996; Smith et al., 2001a). Suspended sediment is an important carrier of contaminants (Quinton and Catt, 2007), and, depending on the soil type and rainfall characteristics, P-enriched soil particles may increase the proportion of PP in surface runoff (McDowell et al., 2001; Miller et al., 2009).

With European policy advocating farm intensification (Department of Agriculture, Food and the Marine, 2013), farmers may have no choice but to spread agricultural waste on land with a high soil P. Land spreading remains the most economical and widespread disposal practice for agricultural wastes (e.g., Nolan et al., 2012). Use of chemical amendments applied to agricultural waste to reduce P losses in surface runoff after land application has been shown to be effective (Smith et al., 2001b; Kalbasi and Karthikeyan, 2004; Moore

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Abbreviations: DM, dry matter; DRP, dissolved reactive phosphorus; DSW, dairy-soiled water; FWMC, flow-weighted mean concentration; PAC, polyaluminum chloride; PP, particulate phosphorus; RCF; relative centrifugal force; SS, suspended solids; TDP, total dissolved phosphorus; TN, total nitrogen; TON, total oxidized nitrogen; WEP, water-extractable phosphorus.

and Edwards, 2007). In contrast to most studies, Brennan et al. (2012) tested the effect of polyaluminum chloride (PAC) [Aln(OH)mCl$_3$n-m; 10% Al_2O_3], alum [$Al_2(SO_4)_3 \cdot nH_2O$; 8% Al_2O_3], or lime [$Ca(OH)_2$] on P and N losses. They found that the three chemicals did not have a significant effect on N losses after the first rainfall event 2 d after slurry application to grassed plots.

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

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

Materials and Methods

Chemical and Physical Analyses

Agricultural Wastes

Total P (TP) was measured using acid persulfate digestion and dissolved reactive P (DRP) by centrifuging at 17,970 relative centrifugal force (RCF) for 5 min, filtering through 0.45-μm filters, and measuring colorimetrically using a nutrient analyzer (Konelab 20, Thermo Clinical Laboratories Systems). Total N was measured using a BioTector TOC TN TP Analyzer (BioTector Analytical Systems Ltd.). Ammonium was extracted from fresh waste by shaking 10 g of waste in 200 mL of 0.1 mol L^{-1} HCl on a peripheral shaker for 30 min at 200 rpm, centrifuging at 17,970 RCF for 5 min, and measuring colorimetrically. Waste pH was measured using a pH probe (WTW), and dry matter (DM) was measured by drying at 105°C for 24 h. All parameters were tested in accordance with the standard methods (APHA, 2005).

Zeolite

The zeolite was sieved to a particle size of 2.36 to 3.35 mm and analyzed for Al_2O_3, BaO, Fe_2O_3, MnO, TiO_2, and SrO using inductively coupled plasma mass spectrometry; CaO, MgO, K_2O, and Na_2O using atomic adsorption spectrometry; P_2O_5 by colorimetry; and SiO_2 by fusion (Vogel, 1989).

Soil

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

Rainfall Simulator Runoff

Runoff samples were tested for pH using a pH probe and for SS using vacuum filtration of at least 50 mL of well-mixed, previously unfiltered subsamples through Whatman GF/C (pore size, 1.2 μm) filter paper (APHA, 2005). Subsamples were filtered through 0.45-μm filters and measured colorimetrically for DRP, NH_4–N, total oxidized N (TON), and nitrite-N (NO_2–N) using a nutrient analyzer (Konelab 20, Thermo Clinical Labsystems). Unfiltered subsamples were tested for TP and total dissolved P (TDP) using acid persulfate digestion and for TN using a BioTector Analyzer (BioTector Analytical Systems Ltd.).

Materials Collection and Characterization

Agricultural Wastes

Three types of agricultural wastes were collected from the Teagasc Research Centre, Moorepark, Fermoy, Co. Cork: (i) dairy slurry from a slatted unit housing dairy cows, (ii) pig slurry from an integrated pig unit, and (iii) DSW from a milking parlor washwater collection sump. Dairy soiled water is defined as dairy wash water from hard standing farmyard areas contaminated with livestock feces, urine, silage effluent, fertilizers and parlor washings, which have a DM content <1% and a 5-d biochemical oxygen demand <2500 mg L^{-1}. All wastes were homogenized immediately before collection by agitating for 30 min using mechanical agitators. The samples were stored in 25-L containers, which were placed in a temperature-controlled room at 11°C for 12 h before the experimental onset. Triplicate samples of each waste were tested for TP, DRP, TN, NH_4–N, pH, and DM (Table 1).

Table 1. Waste characterization for total P, dissolved reactive P, total N, ammonium, pH, and dry matter ($n = 3$). The characterizations were carried out over the full experimental period of the study.

Waste type	TP†	DRP	TN	NH_4–N	pH	DM
	mg L^{-1}					%
Dairy slurry	563 ± 55	18 ± 4	4174 ± 554	1800 ± 16	7.78 ± 0.03	8.0 ± 0.1
Pig slurry	619 ± 30	42 ± 1	2648 ± 242	1814 ± 87	7.49 ± 0.05	2.6 ± 0.1
Dairy-soiled water	52 ± 11	17 ± 1	748 ± 76	163.7 ± 3.0	6.89 ± 0.01	0.7 ± 0.3

† DM, dry matter; DRP, dissolved reactive P; total N, TN; TP, total P.

Zeolite

The zeolite used in this study was of Turkish origin and the sieved zeolite (2.36–3.35 mm), comprised mainly silica (66.7% SiO_2) and aluminum (10.4% Al_2O_3) (Table 2).

Soil

Intact grassed soil samples (500 mm long, 300 mm wide, and 100 mm deep) were collected from grassland that had not received fertilizer application for more than 10 yr in Galway City, Republic of Ireland. The soil was a poorly drained sandy loam (57 ± 5% sand, 29 ± 4% silt, and 14 ± 2% clay) with a Pm of 2.8 ± 0.5 mg kg^{-1} (mg P L^{-1}), a WEP of 2.3 ± 0.4 mg P kg^{-1}, a pH of 6.4 ± 0.3, and an organic matter content of 5 ± 2%. The soil type is classified as an acid brown earth Cambisol (WRB classification).

Adsorption Capacity of Zeolite

The ability of zeolite to remove P (PO_4–P) and N (NH_4–N) from the three types of wastes was first investigated using a multipoint Langmuir isotherm (McBride, 2000):

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

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

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

Optimum Zeolite Application

Bench-scale tests were used to establish optimum application ratios of zeolite (expressed as g zeolite per g DM of waste) for NH_4–N removal for each of the wastes. Sieved zeolite (2.36–3.35 mm) was added ($n = 3$) in amounts ranging from 1 to 15 g to 40 mL of each waste type in 100-mL containers. All containers were sealed and placed on a reciprocating shaker for 24 h at 250 rpm. The samples were then allowed to settle for 1 h, centrifuged at 17,970 RCF for 5 min, and tested for NH_4–N by adding 25 mL of the supernatant to 500 mL of 0.1 mol L^{-1} HCl, shaking for 30 min at 200 rpm, filtering through 0.45-μm filter paper, and measuring colorimetrically. The optimum application ratio was defined as the mass of zeolite above which there was little or no enhanced rate of NH_4–N removal in the supernatant or where the volume of zeolite comprised no greater than 10% of the volume of waste.

To reduce WEP, the following chemicals were mixed with the wastes to which zeolite had been applied at the established optimum ratios for NH_4–N removal: (i) PAC, comprising 10% Al_2O_3 to the dairy slurry at five Al:TP stoichiometric ratios between 0.5:1 and 1.5:1; (ii) PAC, comprising 10% Al_2O_3 to the pig slurry at five Al:TP stoichiometric ratios between 0.3:1 and 1.25; and (iii) alum, comprising $Al_2(SO_4)_3{\cdot}18H_2O$ to the DSW at five Al:TP stoichiometric ratios between 5:1 and 12:1. The combination of amendments that produced the best reductions of NH_4–N concentrations and WEP from the wastes was used in the runoff experiments.

Rainfall Simulation Study

Runoff experiments were conducted in triplicate comparing (i) control soil, (ii) animal wastes, (iii) DSW amended with alum and dairy and pig slurries amended with PAC, and (iv) DSW amended with zeolite and alum and dairy and pig slurries amended with zeolite and PAC. Zeolite was applied at ratios of 2 g g^{-1} DM to the dairy slurry, 6 g g^{-1} DM to the pig slurry, and 10 g g^{-1} DM to the DSW. Polyaluminum chloride was added at stoichiometric ratios of 1.25:1 to the dairy slurry and 1:1 Al:TP to the pig slurry. Alum was added at a stoichiometric ratio of 5:1 Al:TP to the DSW. The waste application rates were 19 kg TP ha^{-1} for pig and dairy slurries and 50 m^3 ha^{-1} for DSW, which equated to 31, 34, and 50 t ha^{-1} for pig and dairy slurries and DSW, respectively. All wastes were mixed for 10 min at 200 rpm using a jar test flocculator and then applied by even and consistent hand spreading in repeated figure-eight patterns to the grassed soil.

Runoff Boxes and Rainfall Simulation

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

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

Table 2. Chemical composition of natural zeolite used. The zeolite was sieved to a particle size of 2.36 to 3.35 mm.

Al_2O_3	BaO	Fe_2O_3	MnO	SiO_2	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	SrO	Loss in ignition at 1000°C
%												
10.4	0.03	0.90	0.01	66.7	1.57	0.52	4.73	0.86	0.06	<0.001	0.04	14.1

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

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

Runoff Analysis

Each of the samples taken at 5-min intervals was tested for pH and for SS. Subsamples, also taken at 5-min intervals, were measured for DRP, NH_4–N, TON, and NO_2–N. Nitrate-N was calculated by subtracting NO_2–N from TON. Unfiltered subsamples, taken at 10, 20, and 30 min after continuous runoff, were tested for TP, TDP, and TN. Dissolved unreactive P was calculated by subtracting DRP from TDP, and PP was calculated by subtracting TDP from TP.

Data Analysis

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

Results

Adsorption Capacity and Bench-Scale Studies

The monolayer adsorption capacity of zeolite, q_{max}, ranged from 0.06 (pig slurry) to 0.31 (dairy slurry) mg P g^{-1} (PO_4–P) and from 0.74 (DSW) to 7.88 (pig slurry) mg N g^{-1} (NH_4–N). The optimum combined amendment application rates for reduction of PO_4–P and NH_4–N for dairy slurry were 2 g g^{-1} DM of zeolite with a stoichiometric PAC ratio of 1.25:1 (Al:TP). The corresponding rates for pig slurry were 6 g g^{-1} DM of zeolite with a stoichiometric PAC ratio of 1:1 (Al:TP) and for DSW were 10 g g^{-1} DM of zeolite with a stoichiometric alum ratio of 5:1 (Al:TP).

Runoff from Laboratory Rainfall Simulation Study

Phosphorus

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

Nitrogen

The FWMCs for TN from the control soil ranged from 8.5 (RE1) to 11 mg L^{-1} (RE3). The TN concentrations in runoff were observed to increase for all unamended slurry applications compared with the control soil ($p < 0.001$). Ammonium-N concentrations were highest for pig slurry, followed by dairy slurry and DSW, whereas TON concentrations in runoff, primarily as NO_3–N, were highest for dairy slurry, followed by pig slurry and DSW (Table 3). The FWMCs of TN, NH_4–N, and NO_3–N in runoff for chemically amended wastes (without zeolite addition) over the three rainfall events were reduced by 40, 57, and 45% (dairy slurry); 13, 0, and 0% (pig slurry); and 8, 32, and 26% (DSW) compared with unamended wastes. Application of combined zeolite and chemical amendments further reduced TN, NH_4–N, and NO_3–N concentrations in runoff from all three wastes over the three rainfall events to below those achieved by chemical amendments only (Fig. 2). Decreases in TN of amended wastes compared with unamended wastes were significant for all treatments except for alum-amended DSW and PAC-amended pig slurry ($p < 0.001$). The TN concentrations in runoff using with dual zeolite and PAC/alum amendments were less than those using PAC/alum amendments only for all wastes ($p < 0.001$). The combined amendments reduced NO_3–N concentrations in runoff below those of unamended wastes by 49% for dairy slurry (325–167 μg L^{-1}), 31% for pig slurry (168–115 μg L^{-1}), and 38% for DSW (42–26 μg L^{-1}).

Suspended Solids

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

The average FWMC of PP in runoff was highly correlated with corresponding SS concentrations for dairy slurry (R^2 =

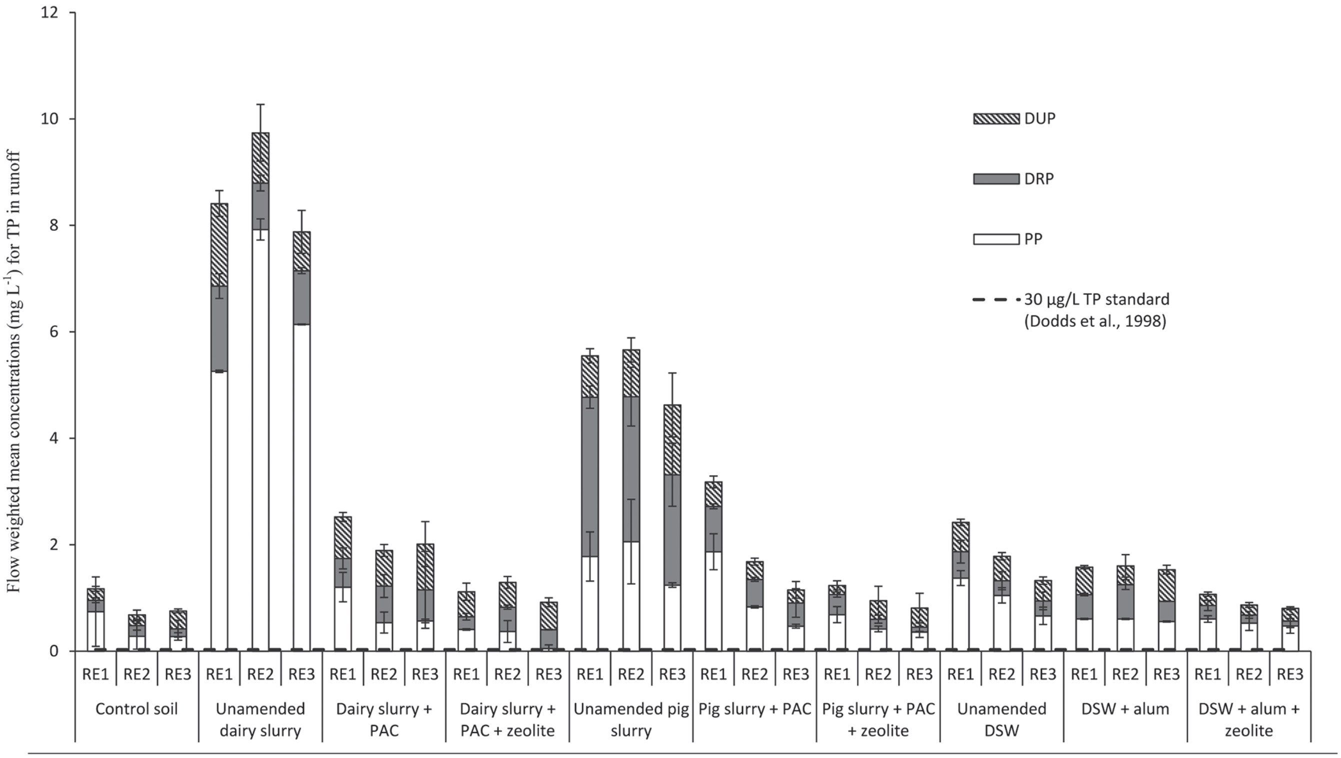

Fig. 1. Histogram of flow-weighted mean concentrations for total P (TP) comprising particulate P (PP), dissolved reactive P (DRP), and dissolved unreactive P (DUP) in runoff from rainfall event 1 (RE1) at *t* = 72 h, rainfall event 2 (RE2) at *t* = 92 h, and rainfall event 3 (RE3) at *t* = 120 h. Data regarding TP standard are from Dodds et al. (1998). DSW, dairy-soiled water; PAC, polyaluminum chloride.

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

pH

Over the three rainfall events, the average pH in runoff from PAC-amended dairy slurry was lower than unamended dairy slurry (Table 3). There was no significant difference in pH between unamended and PAC-amended pig slurry and unamended and alum-amended DSW (Table 3). The average pH in runoff over the three rainfall events from dairy and pig slurries amended with zeolite and PAC was lower than that

Table 3. Flow-weighted mean concentrations in runoff averaged over three rainfall events and percent reductions from unamended slurries for total P, particulate P, total dissolved P, dissolved reactive P, dissolved unreactive P, total N, ammonium, nitrite, nitrate, suspended solids, and pH and % reduction or increase from unamended waste pH in runoff.

Waste application†	TP‡	PP	TDP	DRP	DUP	TN	NH_4–N	NO_2–N	NO_3–N	SS	pH	% reduction (−)/increase (+) from unamended slurry pH in runoff
	————	————	————	mg L^{-1}	————	————	————	µg L^{-1}		mg L^{-1}		
Control soil	0.87	0.43	0.44	0.19	0.25	9.64	3.37	9	36	27	6.43	–
D(U)	8.68	6.44	2.23	1.16	1.07	41.00	16.53	380	325	535	6.73	–
D(CA)	2.14 (75)§	0.77 (88)	1.37 (39)	0.60 (48)	0.77 (28)	25.54 (40)	7.11 (57)	179 (53)	180 (45)	198 (63)	6.30	−6.4
D(A)	1.11 (87)	0.28 (96)	0.83 (63)	0.35 (70)	0.48 (55)	18.08 (56)	5.25 (68)	131 (66)	167 (49)	143 (73)	6.37	−5.4
P(U)	5.28	1.69	3.59	2.60	0.99	41.02	26.10	42	168	101	6.58	–
P(CA)	2.00 (62)	1.06 (38)	0.95 (74)	0.60 (77)	0.35 (65)	35.56 (13)	26.65	62	175	52 (49)	6.67	1.3
P(A)	1.00 (81)	0.49 (71)	0.51 (86)	0.22 (92)	0.29 (70)	22.48 (45)	13.95 (47)	42 (1)	115 (31)	57 (44)	6.21	−5.6
DSW(U)	1.84	1.03	0.81	0.35	0.46	25.95	12.43	11	42	112	6.08	–
DSW(CA)	1.57 (15)	0.59 (43)	0.98	0.49	0.49	23.98 (8)	8.46 (32)	13	31 (26)	48 (57)	5.93	−2.5
DSW (A)	0.92 (50)	0.54 (48)	0.38 (53)	0.17 (53)	0.21 (54)	14.33 (45)	3.37 (73)	14	26 (38)	85 (25)	6.95	14.3

† D(A), dairy slurry amended with zeolite at 2 g g^{-1} dry matter (DM) (160 kg m^{-3}) and polyaluminum chloride (PAC) at 1.25:1 Al:total P (TP) (704 mg L^{-1}); D(CA), dairy slurry amended with PAC at 1.25:1 Al:TP (704 mg L^{-1}); DSW(A), dairy-soiled water amended with zeolite at 10 g g^{-1} DM (70 kg m^{-3}) and alum at 5:1 Al:TP (260 mg L^{-1}); DSW(CA), dairy-soiled water amended with alum at 5:1 Al:TP (260 mg L^{-1}); DSW(U), unamended dairy-soiled water; D(U), unamended dairy slurry; P(A), pig slurry amended with zeolite at 6 g g^{-1} DM (156 kg m^{-3}) and PAC at 1:1 Al:TP (619 mg L^{-1}); P(CA), pig slurry amended with PAC at 1:1 Al:TP (619 mg L^{-1}); P(U), unamended pig slurry.

‡ DRP, dissolved reactive P; DUP, dissolved unreactive P; PP, particulate P; SS, suspended solids; TDP, total dissolved P; TP, total P.

§ Values in parentheses are % reduction.

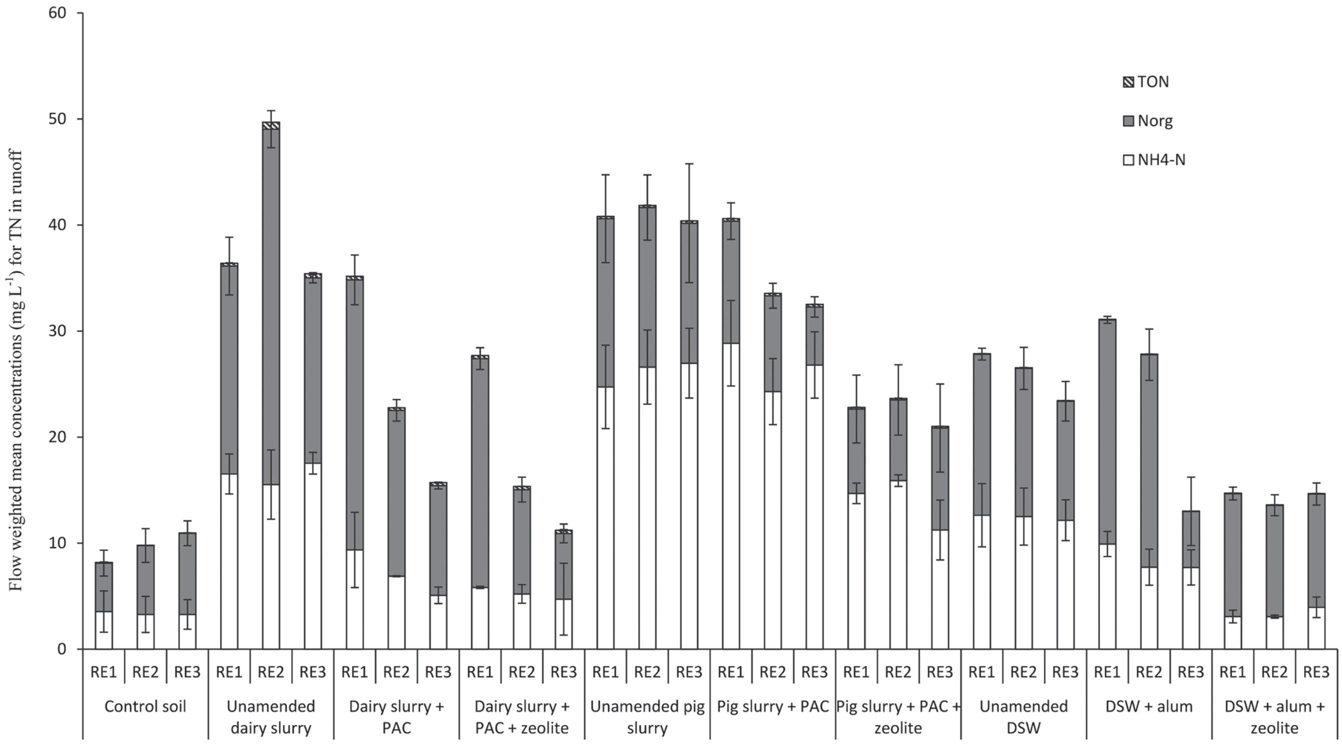

Fig. 2. Histogram of flow-weighted mean concentrations for total N (TN) comprising NH_4–N, organic N (N_{org}), and total oxidized N (TON) in runoff from rainfall event 1 (RE1) at *t* = 72 h, rainfall event 2 (RE2) at *t* = 92 h, and rainfall event 3 (RE3) at *t* = 120 h. DSW, dairy-soiled water; PAC, polyaluminum chloride.

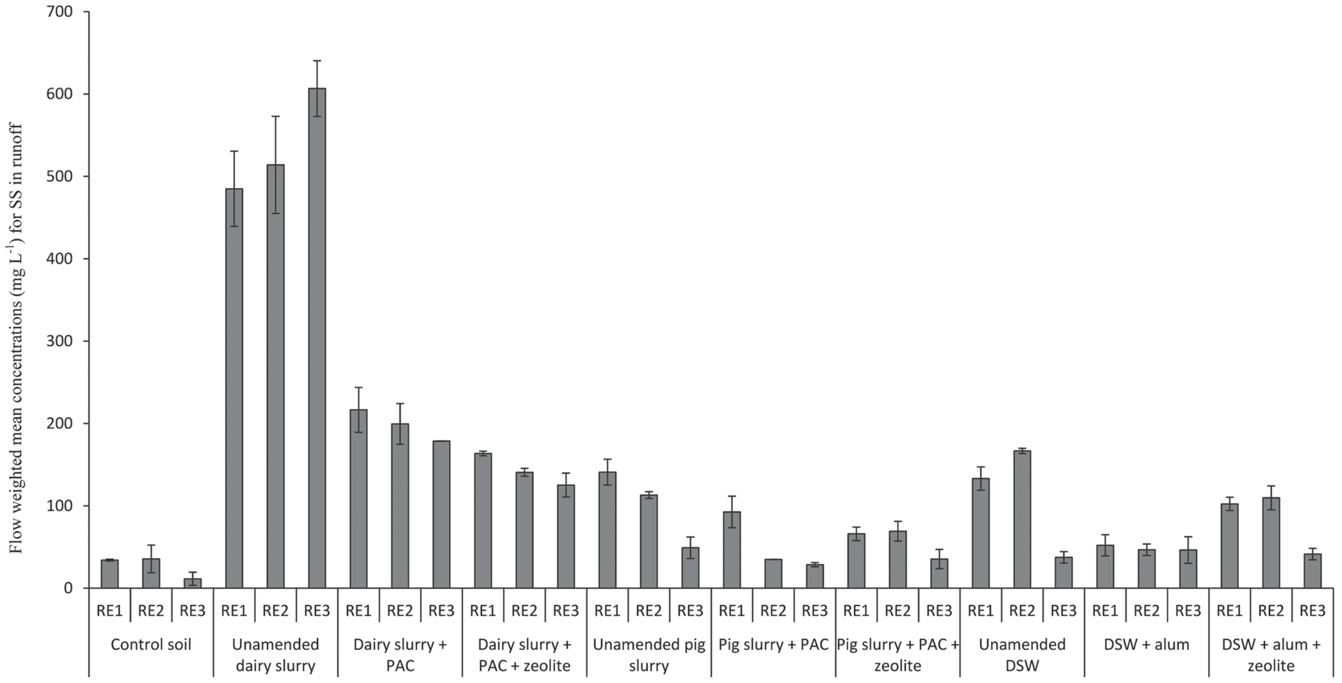

Fig. 3. Histogram of flow-weighted mean concentrations for suspended sediment (SS) in runoff from rainfall event 1 (RE1) at *t* = 72 h, rainfall event 2 (RE2) at *t* = 92 h, and rainfall event 3 (RE3) at *t* = 120 h. DSW, dairy-soiled water; PAC, polyaluminum chloride.

for unamended slurries but was higher in runoff from DSW amended with zeolite and alum.

Discussion

The amendments used in this study had specific removal capacities, predominantly zeolite for N removal and PAC/alum for P and SS removal. The combinations used were those that produced the best reductions of NH_4–N and WEP from the wastes (optimum zeolite application). The use of packed soil boxes and simulated rainfall is recognized as a practical, if limited, method to assess P transport from grassed and bare soils (Sharpley and Kleinman, 2003; Kleinman et al., 2004).

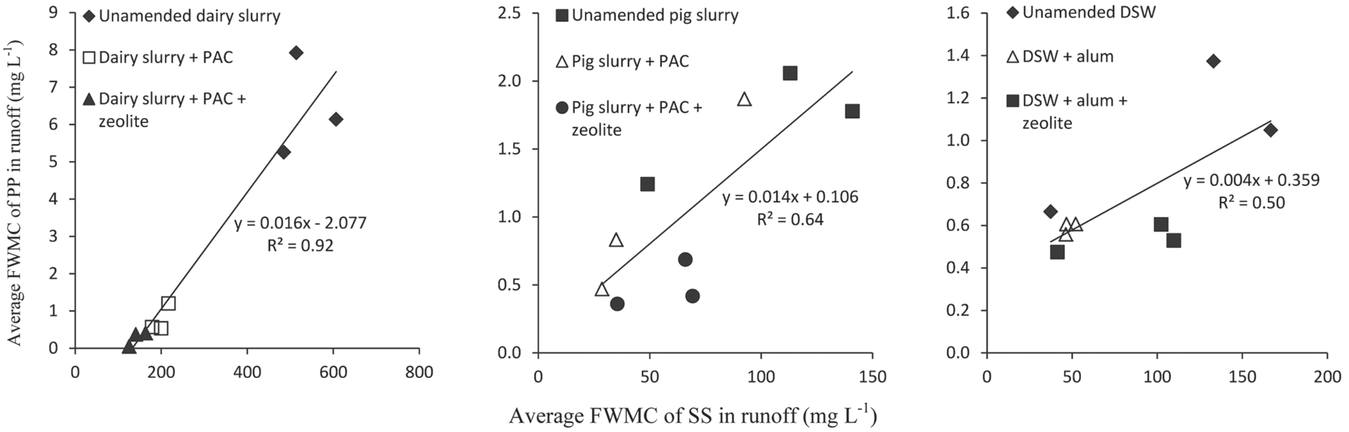

Fig. 4. Correlation between suspended solid (SS) concentrations and corresponding particulate P (PP) concentrations for dairy slurry, pig slurry, and dairy-soiled water (DSW) averaged over all three rainfall events. The data include unamended wastes, wastes amended with polyaluminum chloride (PAC)/alum only (no zeolite), and combined zeolite and PAC/alum amendments. Lines represent a least squares regression analysis, with R^2 values indicated.

Phosphorus in Runoff

Observed reductions in P using only PAC/alum amendments (without zeolite) were generally consistent with previous studies (Smith et al., 2001b; Elliott et al., 2005; O'Rourke et al., 2012). The average concentrations of TP in runoff after application of unamended dairy slurry increased from 0.87 to 8.7 mg L^{-1} for the control soil. This is consistent with the findings of Preedy et al. (2001), who recorded peak TP concentrations of 7 mg L^{-1} from dairy slurry (6% DM) exposed to 28 d of intermittent rainfall ranging in intensity from 0.2 to 3 mm h^{-1} rainfall in a lysimeter plot study. The reduced runoff concentrations in TP and DRP for dairy slurry using PAC at a ratio of 1.25:1 Al:TP (87 and 70%, respectively) were similar to those reported by Hanrahan et al. (2009) (89 and 65%, respectively) at a time interval of 5 d between application of dairy waste and a simulated rainfall event. In the current study, reductions in TP for dairy slurry are dominated by reductions in PP (6.44–0.77 mg L^{-1}), and the average FWMCs of PP and SS in runoff were related to one another (Fig. 4). The comparatively high DM content of dairy slurry compared with the other wastes (Table 1) meant that, when applied to the soil, much of it remained on the surface for the duration of the experiment. This contrasted with the pig slurry and DSW, which infiltrated the soil quite quickly after application because of their lower DM contents. The position of the dairy slurry on the soil facilitated a higher direct exposure to rainfall compared with the other applied wastes and resulted in higher runoff SS (Fig. 3) and PP concentrations (Fig. 1). Eroded P-enriched particles can be mobilized by rain splash detachment, flow detachment, or dispersion (Miller et al., 2009) and may be transported significant distances (Sharpley et al., 1999). Our results indicate that suspended dairy slurry solids, as opposed to soil solids, may be the principal transport mechanism for runoff P, predominantly as PP, from unamended slurry. The addition of PAC and PAC/zeolite to the dairy slurry reduced SS and PP concentrations. It is likely that release of Al^{3+} flocculants from the PAC reduced the extent of fragmentation of the slurry into primary particles, hence reducing the concentration of SS transported by overland flow. The ratio of PP:TP reduced from 0.74 for unamended slurry to 0.36 for PAC amended slurry and 0.25 for combined zeolite and PAC-amended dairy slurry, confirming that PAC, not zeolite, is the most effective of the two amendments in binding PP.

The SS concentrations in runoff from unamended pig slurry were much lower than those of unamended dairy slurry, as were the TP concentrations. The correlation between PP and SS for pig slurry was not as strong as for dairy slurry (Fig. 4). This was likely due to the lower DM content of the pig slurry (Table 1). As a consequence, it is likely that the same opportunity for particle segregation from the slurry was not available and thus PP in runoff was not as prevalent as for dairy slurry (PP:TP = 0.32). The addition of PAC amendment only (no zeolite) increased the PP:TP ratio to 0.53, whereas the ratio for dual zeolite and PAC was similar (0.49). The overall DRP removal rates for pig slurry were similar to those of previous studies. In a runoff experiment to evaluate the impact of alum and aluminum chloride on swine manure applied to small grassed plots, Smith et al. (2001b) observed DRP reductions of 4.6 mg L^{-1} in runoff between unamended manure and manure treated with 1:1 Al:TP molar ratio. This represented an 84% reduction in DRP and is comparable to the 77% reduction measured in the current study using PAC at the same ratio. The removal rates in the current study increased to 92% when combined zeolite and PAC amendments were applied.

Very few data exist on runoff P concentrations from DSW applied to grassed soil under simulated rainfall conditions. In a study to measure the effects of rainfall events on P and SS losses from a grassed soil, Serrenho et al. (2012) reported an TP reduction of approximately 80% from relatively dilute DSW (DM = 0.2%; TP = 14.2 mg L^{-1}) amended with alum at a stoichiometric ratio of 8.8:1. They reported a weak correlation ($R^2 = 0.15$) between PP and SS in runoff for the unamended DSW but a high PP:TP ratio of 0.75. In the current study, a lower stoichiometric ratio (5:1) of alum amendment resulted in a lower TP reduction of 15% for a stronger DSW than that of Serrenho et al. (2012) (Table 1). It is likely that application of the higher alum ratio by Serrenho et al. (2012) was more successful in sorbing dissolved P to the soil than in the current study, and P-enriched soil particles were then mobilized in runoff. In the current study, both alum and dual zeolite and alum amendments resulted in similar reductions in PP (43 and 48%, respectively) compared with unamended DSW. Use of alum only (no zeolite) did not reduce dissolved P below that of unamended waste. In contrast, dual application of zeolite and alum reduced both DRP and dissolved unreactive P by 53%, indicating that zeolite may have contributed to dissolved P removal in runoff from DSW. The PP:TP ratios for the unamended DSW, alum amended DSW, and dual zeolite and alum amended DSW were 0.56, 0.38, and 0.59, respectively. These results, combined with the weak correlation between PP and SS in runoff (Fig. 4), suggest that dissolved P losses may be just as significant as PP losses for the rates of amendments used.

Nitrogen in Runoff

The results of this study confirm the results of previous studies using specific amendments in the treatment of agricultural wastes for N (Nguyen and Tanner, 1998; Widiastuti et al., 2011). The observed reductions in runoff NH_4–N compared with unamended wastes were highest for pig slurry, followed by dairy slurry and DSW (Table 3). The reduction in NH_4–N in runoff from dairy slurry amended with PAC (57%) compared with unamended dairy slurry was consistent with the findings of Brennan et al. (2012) (62%). Application of combined zeolite and PAC/alum amendments reduced NH_4–N concentrations in runoff to approximately those of the control soil (3.37 mg L^{-1}) for dairy slurry (5.25 mg L^{-1}) and DSW (3.37 mg L^{-1}) but not for pig slurry (13.95 mg L^{-1}).

The physical composition of the three wastes (Table 1) and their appearance on the grassed soil was quite different. Whereas dairy slurry remained on top of the grassed soil, both the pig slurry and DSW infiltrated it more easily. Torbert et al. (2005) observed that the interaction between the applied manure and runoff water is of primary importance for the loss of pollutants. A high interaction between the grass thatch layer and the manure will greatly reduce the amount of manure that leaves the grassed soil as particles but also increases the interaction that the runoff water has with the surface area of the manure. Although grass was cropped to approximately 25 mm in this study, it is likely that the zeolite benefited from more contact time with the dairy slurry than with either the pig slurry or DSW, and this may have resulted in the lower NH_4–N in runoff for the dairy slurry. Conversely, the interaction time between the zeolite and pig slurry may have been insufficient to achieve a similar level of NH_4–N removal as measured for dairy slurry. We are not sure why the NH_4–N runoff removal rate for DSW was so high, but it may be possible that the alum sequestered some ammonia or that pockets of DSW may have pooled on parts of the saturated soil surface, thereby facilitating a higher contact time with the zeolite. The NH_4–N concentrations for pig and dairy slurries were 1800 mg L^{-1}, whereas that of the DSW was much lower at 164 mg L^{-1}, and this also may have influenced concentrations of NH_4–N in runoff.

Loss of NH_4–N from land-applied wastes is of interest because such losses greatly reduce the fertilizer values of slurry (Misselbrook et al., 2002). More than 50% of applied N can be lost by ammonia volatization, with close to 50% of these emissions occurring in the first 24 h during and after slurry application (Sommer and Hutchings, 2001; Sommer et al., 2003). In an experiment to assess the effects of alum or zeolite addition to dairy slurry on ammonia volatization, Lefcourt and Meisinger (2001) found that 65% of ammonia emissions in unamended slurry occurred within 24 h of exposure. Addition of alum at rates of 2.5 and 6.25% reduced these losses by 58 and 57%, respectively, compared with unamended controls, with most of the losses occurring in the initial 12 h and negligible losses thereafter. In the same experiment, addition of zeolite, also at rates of 2.5 and 6.25%, reduced ammonia emissions by 22 and 47%, respectively, compared with the unamended controls, with most of the losses occurring in the initial 24-h period and at a reduced rate thereafter. Although the modes of ammonia capture were different for both types of amendments (acidification for alum [Bussink et al., 1994] and availability of NH_4–N exchange sites for zeolite), ammoniacal capture occurred mostly within a 24-h period for both amendments, albeit at a much slower rate for zeolite. In the current study, the zeolite and chemical amendments were added immediately before application of the wastewaters to the runoff boxes, and it is likely that some ammonia may have volatilized in the initial 48-h period before the rainfall simulation took place. It may be beneficial, therefore, on a practical basis to add the zeolite to the wastewaters at least 24 h and chemicals at least 12 h before landspreading to facilitate reduced ammonia volatilization.

Suspended Sediment in Runoff

Suspended sediment in runoff from the control soil was 0.99 kg ha^{-1}, and the largest increases after application of unamended wastes were for dairy slurry (19.5 kg ha^{-1}), followed by DSW (4.7 kg ha^{-1}) and pig slurry (4.0 kg ha^{-1}). The large increase for dairy slurry is consistent with its relatively high DM content compared with the other wastes (Table 1), and all SS fluxes were likely to have been influenced by the wet antecedent soil conditions. Reductions in runoff SS were highest when all three wastes were amended with PAC/alum only (no zeolite) (Table 3). These removal rates did not change significantly for dairy and pig slurries when amended with dual zeolite and PAC but were reduced for DSW when amended with dual zeolite and alum. This suggests that SS reduction is predominantly due to the release of flocculants from the PAC/alum, which aids adhesion of the SS in the wastes and in the soil, thereby decreasing their susceptibility to loss in runoff. We are not sure why there was an increase in SS concentrations for the DSW when amended with dual zeolite and alum, and it is interesting to note that there was no corresponding increase in PP or any of the other P fractions (Table 3). One possible explanation for this is that the increased SS release might have been mainly in the form of sand released from the soil (the soil comprised 57% sand), with a corresponding lower P adsorption capacity than either the silt or clay fractions (Hansen et al., 2002).

Cost Analysis of Amendments

A preliminary cost analysis on the use of dual zeolite and PAC/alum amendments indicates that high costs, particularly the cost of zeolite, may be a prohibitive factor regarding their widespread application. Taking the cost of amendments only (without the ancillary costs of storage, application, mixing, and spreading) at €1,150 t^{-1} for zeolite (in Ireland), €480 t^{-1} for PAC, and €250 $tonne^{-1}$ for alum, the costs per cubic meter of applied slurry based on application rates used in this study are €190 for dairy slurry, €188 for pig slurry, and €84 for DSW. These compare with estimated costs per cubic meter of €6.40 for dairy slurry, €5.60 for pig slurry, and €0.80 for DSW using PAC/alum amendments only (Brennan et al., 2011). Therefore, the additional cost of using dual zeolite and chemical amendments is significantly higher than the use of chemical only (by an order of magnitude in excess of 2 in the case of DSW) and consequently may not be an attractive mitigation option in areas where zeolite is not an indigenous natural material and where purchase costs may be prohibitive. Acknowledging that final costs may vary with location and availability of zeolite, it is nevertheless unlikely that widespread use of dual zeolite and chemical amendments in agricultural wastewaters will be economically sustainable in the short to medium term and would be better suited to critical source areas (areas where there is a high risk of incidental losses in overland flow) or where land availability for spreading agricultural wastes is limited.

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Appendix B

Journal of Environmental Quality TECHNICAL REPORTS

SURFACE WATER QUALITY

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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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

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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 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

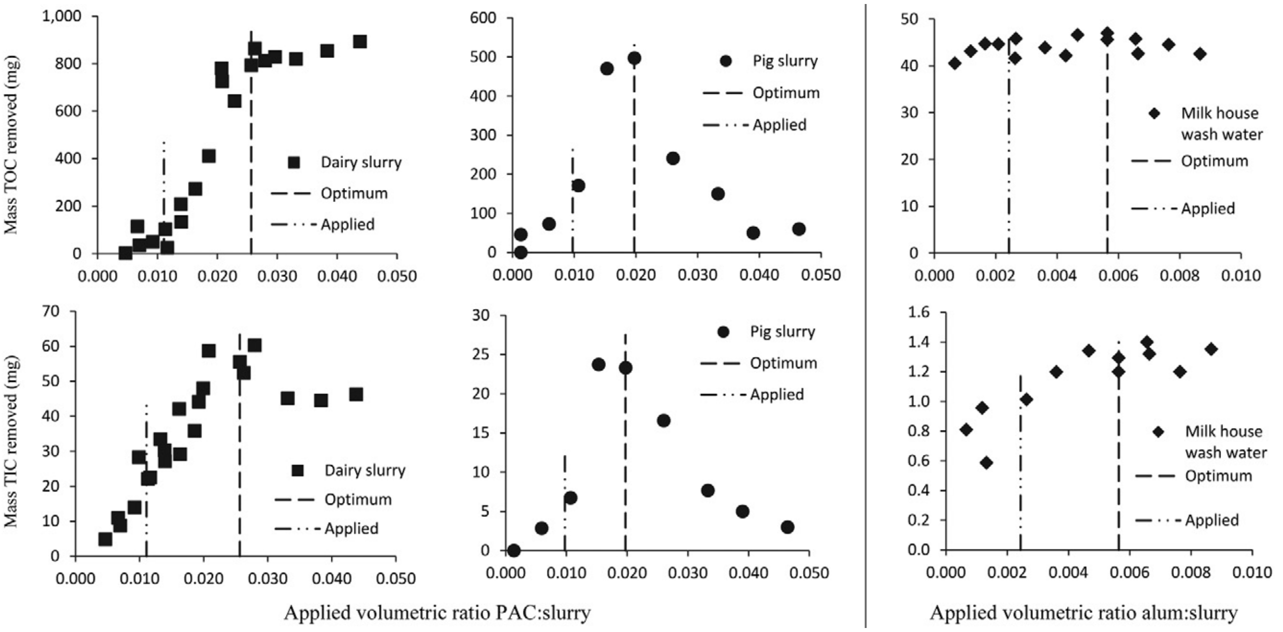

Fig. 1. Total organic C (TOC) and total inorganic C (TIC) removal in batch study tests (*n* = 3) after application of polyaluminim chloride (PAC) to dairy and pig slurries and alum to milk house wash water (MWW). Optimum volumetric ratios for TOC and TIC removals were 0.0256 and 0.0197 PAC/slurry for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

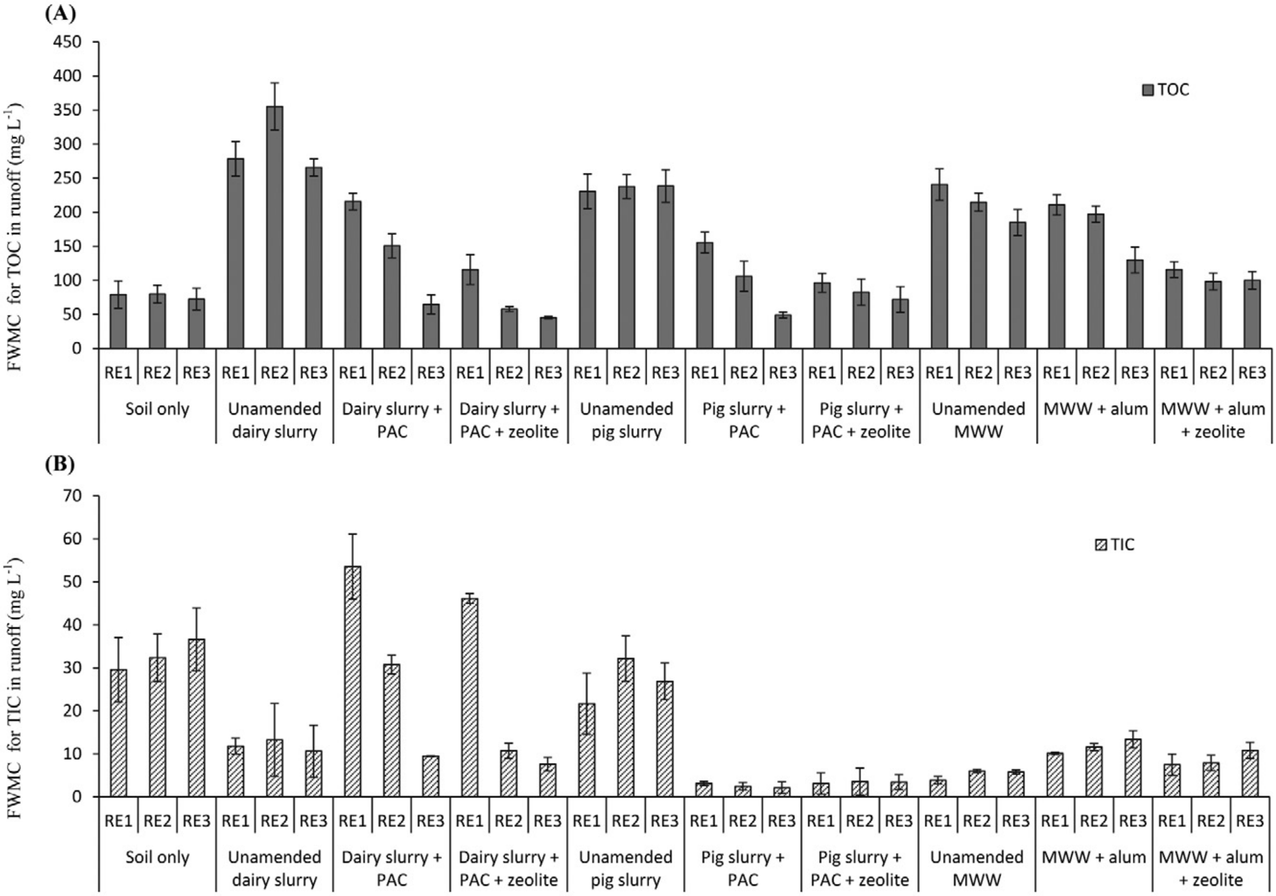

Fig. 2. Histogram of flow-weighted mean concentrations (FWMCs) ($n = 3$) for (A) total organic C (TOC) and (B) total inorganic C (TIC) in runoff from rainfall event 1 (RE1) at t = 72 h, rainfall event 2 (RE2) at t = 92 h, and rainfall event 3 (RE3) at t = 120 h. Error bars indicate SD.

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)	105ab	51	9bc	−68

† D(P), dairy slurry amended with polyaluminum 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.

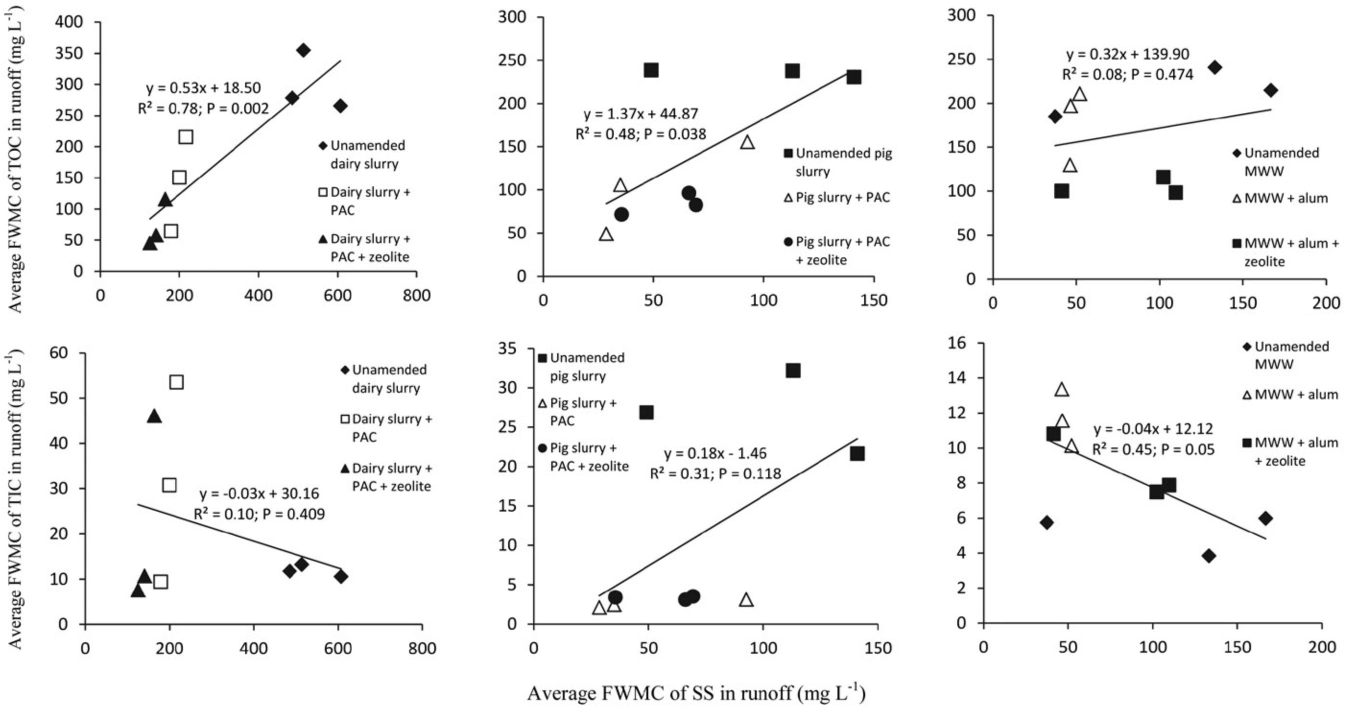

Fig. 3. Correlation between suspended solids (SS) concentrations and corresponding total organic C (TOC) and total inorganic C (TIC) concentrations (n = 3) for dairy slurry, pig slurry, and milk house wash water (MWW) averaged over all three rainfall events. The data include unamended wastes, wastes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

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Assessment of intermittently loaded woodchip and sand filters to treat dairy soiled water

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ABSTRACT

Land application of dairy soiled water (DSW) is expensive relative to its nutrient replacement value. The use of aerobic filters is an effective alternative method of treatment and potentially allows the final effluent to be reused on the farm. Knowledge gaps exist concerning the optimal design and operation of filters for the treatment of DSW. To address this, 18 laboratory-scale filters, with depths of either 0.6 m or 1 m, were intermittently loaded with DSW over periods of up to 220 days to evaluate the impacts of depth (0.6 m versus 1 m), organic loading rates (OLRs) (50 versus 155 g COD m^{-2} d^{-1}), and media type (woodchip versus sand) on organic, nutrient and suspended solids (SS) removals. The study found that media depth was important in contaminant removal in woodchip filters. Reductions of 78% chemical oxygen demand (COD), 95% SS, 85% total nitrogen (TN), 82% ammonium-nitrogen (NH_4–N), 50% total phosphorus (TP), and 54% dissolved reactive phosphorus (DRP) were measured in 1 m deep woodchip filters, which was greater than the reductions in 0.6 m deep woodchip filters. Woodchip filters also performed optimally when loaded at a high OLR (155 g COD m^{-2} d^{-1}), although the removal mechanism was primarily physical (i.e. straining) as opposed to biological. When operated at the same OLR and when of the same depth, the sand filters had better COD removals (96%) than woodchip (74%), but there was no significant difference between them in the removal of SS and NH_4–N. However, the likelihood of clogging makes sand filters less desirable than woodchip filters. Using the optimal designs of both configurations, the filter area required per cow for a woodchip filter is more than four times less than for a sand filter. Therefore, this study found that woodchip filters are more economically and environmentally effective in the treatment of DSW than sand filters, and optimal performance may be achieved using woodchip filters with a depth of at least 1 m, operated at an OLR of 155 g COD m^{-2} d^{-1}.

1. Introduction

Dairy soiled water (DSW) (variously referred to as dairy effluent (Longhurst et al., 2000; McFarland et al., 2003), dairy dirty water (Cannon et al., 2000; Moir et al., 2005), or milk-house washwater (Joy et al., 2001)), is a variable strength dairy effluent (typical range 1000–10 000 mg 5-day biochemical oxygen demand (BOD_5) L^{-1}) comprising milking parlour and holding area washings generated in large but variable volumes (27–148 L cow^{-1} d^{-1}), and is characterised by low dry matter (DM) content (typically < 3–4%). Nutrient concentrations in DSW vary considerably, typically between 70 and 500 mg total nitrogen (TN) L^{-1} and 20 to >100 mg total phosphorus (TP) L^{-1} (Minogue et al., 2015). The volume and strength of DSW is seasonal and depends on farm management practices, including the efficiency of milking systems (Sweeten and Wolfe, 1994), size of herd, and amount of rainfall-generated runoff from uncovered hard standings (Minogue et al., 2015). Dairy soiled water is collected separately from dairy slurry and the main disposal route is directly to land via landspreading or irrigation without any prior treatment. Because of its high volume and often unpredictable composition, DSW is frequently perceived to be of little or no agronomic benefit and is often applied repeatedly to land adjacent to the milking parlour (Wang et al., 2004). Storage of DSW is required at locations where landspreading is restricted due to adverse weather conditions, soil type, soil conditions, ground slope, proximity to water sources, and volumetric spreading

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limitations. In Ireland, for example, there is a legal requirement to provide a DSW storage capacity of 10–15 days (S.I. No. 31 of 2014), which results in increased infrastructure and associated costs for the dairy farmer. These costs, combined with the low nutrient replacement value of the DSW, mean that treatment and reuse may be a better option for the farmer.

The environmental impacts of repeated spreading of DSW on lands are well documented (e.g. Fenton et al., 2011), and may result in oxygen depletion and asphyxiation of aquatic life in surface waters, as well as a risk of nutrient leaching to groundwater (Knudsen et al., 2006). Long-term DSW application to lands may also result in soil accumulation of phosphorus (P) and heavy metals and increase concentrations of microbial pathogens, odorants and oestrogens in the receiving environment (Wang et al., 2004; Hao et al., 2008). Hence, there is a real need for cost-effective, low energy, and low maintenance on-farm treatment processes that would result in a reduced risk of pollution following application to land. Some multi-stage biological treatment processes, such as combined sequencing batch reactors (SBRs) and constructed wetlands (CWs) (Moir et al., 2005), and aerated settling tanks followed by vertical flow CWs (Merlin and Gaillot, 2010), have been used with varying degrees of success; however, much of the organic and nutrient reductions in these studies have been reported to occur in the aeration rather than in the passive processes. Passive treatment systems such as sand filters (Rodgers et al., 2005; Healy et al., 2007) and woodchip filters (Ruane et al., 2011; McCarthy et al., 2015) have also been investigated and have reported consistently high levels of organic, nutrient and pathogenic removal. Woodchip, in particular, is a cheap, biodegradable material which has potential use as a soil improver (Cogliastro et al., 2001; Miller and Seastedt, 2009) and has previously shown to be effective in improving effluent quality and ammonia emissions when used in out-wintering pads (Dumont et al., 2012).

In order to realise the full potential of woodchip filters, it is necessary to determine the optimum media depths which will produce consistently high quality effluent when subjected to variable strength influent DSW loading. Filters are usually designed and operated with one hydraulic regime selected to deliver an optimum organic loading rate (OLR). However, as the concentration of DSW varies seasonally (Rodgers et al., 2005), woodchip filters may be subjected to OLRs far in excess of their design capacity. Therefore, it is necessary to examine the performance of filters under these extreme conditions. Limited information is available on the impact of woodchip filter depths and OLRs on the quality of treated DSW effluent. Additionally, no information is available on the comparative performances of woodchip and sand filters when treating on-farm DSW.

As there are still knowledge gaps concerning the optimal design and operation of woodchip filters for the treatment of DSW, including the appropriate OLR and filter depth for optimal performance, the objectives of this study were to examine the impacts of filter depth and OLR on their performance when loaded with DSW and to compare them to sand filters operated under the same experimental conditions. An overarching objective of the study was to contribute to an improved understanding of the factors which should be considered in the design, construction and management of passive woodchip filters to treat on-farm DSW. Once such factors are resolved, pilot-scale filters may be effectively operated on the farm.

2. Materials and methods

Eighteen filters, with internal diameters of 0.1 m and depths of either 0.6 m (n = 3 columns) or 1 m (n = 15 columns), were constructed using uPVC. All filters were open at the top and sealed at the base using uPVC end caps. The columns were placed on timber support frames and located in a temperature-controlled room at 10.6 ± 0.7 °C and relative humidity of 86.9 ± 4.5% (replicating the average temperature and humidity in Ireland). A 0.075 m layer of clean, crushed pea gravel, manually sieved to a particle size of 10–14 mm, was placed at the base of each column to prevent washout of the filter media. Each column was then filled with either woodchip (with a particle size of 10–20 mm) or sand (effective size, $d_{10} = 0.2$, uniformity coefficient, UC = 1.4) by placing the selected media in 0.050 m lightly tamped increments. Influent DSW was pumped intermittently (four times per day, seven days per week) onto the filters using peristaltic pumps controlled by electronic timers. Hydraulic loading rates were adjusted using the manual flow control on the pumps and influent was distributed evenly across the surface of the filter media using perforated uPVC flow distribution plates (Fig. 1). Continuously operated submersible mixers were placed in each DSW influent container (one container per column set) to prevent stratification. Treated effluent samples from each filter were collected in an effluent collection container and all influent DSW samples were taken simultaneously from the influent containers.

To clean any organic material from the media, 70 L of potable water was pumped onto each filter over a period of 5 days prior to their operation, before being intermittently loaded with DSW for a period of 56 days. On day 15 of operation, each filter was seeded with 500 mL of nitrifying activated sludge (mixed liquor suspended solids, MLSS = 6290 mg L^{-1}; sludge volume index, SVI = 143) collected from a local wastewater treatment plant. The period from day 0–56 was taken as the start-up period to reach steady state operation (defined by consistent chemical oxygen demand (COD), N and P effluent concentrations) for all filters and therefore day 56 was taken as the effective start day of the study (day 0).

This study compared three different operational setups to examine the impacts of (1) filter depth (2) OLR and (3) type of media (woodchip/sand) on filter performance. The filter configurations (Fig. 2) were (1) 0.6 and 1 m deep woodchip filters operating for 105 days with an average OLR of 120 g COD m^{-2} d^{-1} (2) 1 m deep woodchip filters operating for 105 days with average OLRs of 50 and 155 g COD m^{-2} d^{-1}, and (3) 1 m deep woodchip and sand filters operating for 220 days with an average OLR of 35 g COD m^{-2} d^{-1}. All configurations and treatments were constructed and operated at n = 3. The very high OLRs (120 and 155 g COD m^{-2} d^{-1}) were selected to assess the performance of filters under extreme loading events, which may arise if a filter is designed and hydraulically loaded assuming a low influent organic concentration.

Dairy soiled water was collected weekly for the duration of the experiments in 25 L capacity containers from a dedicated DSW collection tank at a 150 cow dairy farm in south west Ireland (51°37′35.8″N 8°46′06.6″W). A submersible pump was used to fill the containers, which were then transferred directly to a temperature-controlled room in the laboratory. The average physical and chemical characteristics of the influent DSW are shown in Table 1.

The woodchip used was a commercial tree species, Sitca spruce (*Picea sitchensis*). Logs were debarked and then chipped using an industrial wood chipping machine (Morbark post peeler) at an industrial facility in northwest Ireland. The woodchips were sieved to a 10–20 mm grading prior to placing in the filter columns. The sand used was sourced from a commercial quarry in Co. Galway, West of Ireland and was graded to a d_{10} of 0.2 mm and a UC of 1.4. The permeability of the saturated woodchip and sand (Table 2) was measured using the constant head permeability test in accordance with BS 1377-5 (BSI, 1990).

The ability of the woodchip and sand media to remove N

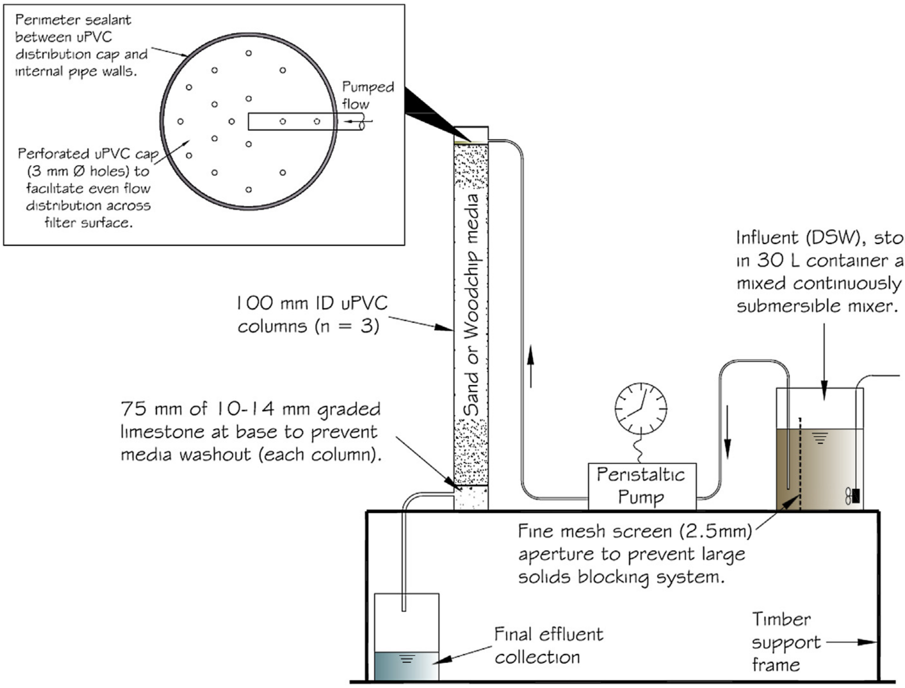

Fig. 1. Schematic diagram of typical laboratory filter setup. (Not to scale).

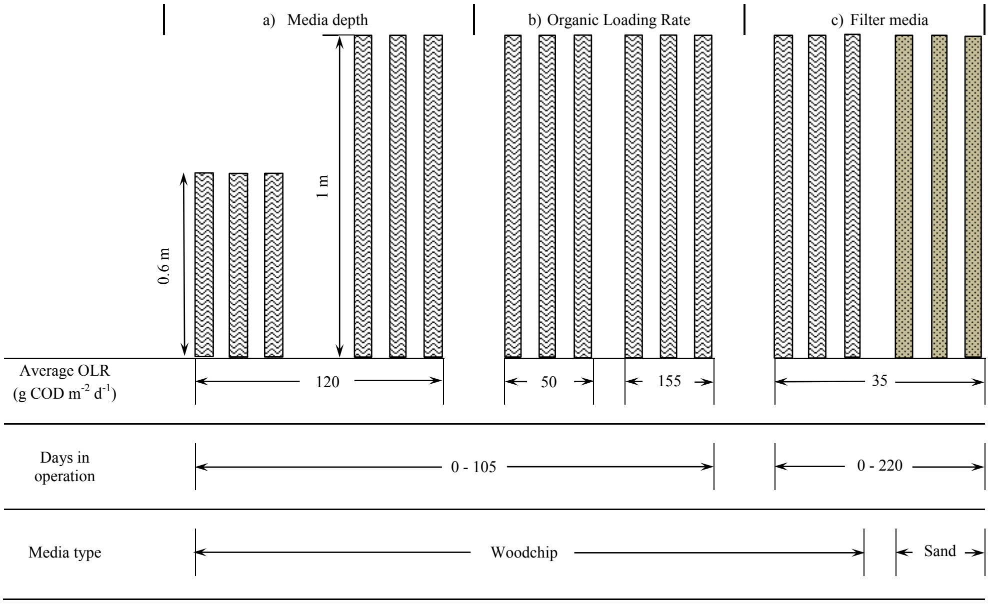

Fig. 2. Combinations of a) media depth, b) organic loading rates and c) filter media used in this study. The woodchip used was 10–20 mm Sitka spruce (picea sitchensis). The sand used had a d_{10} = 0.2 mm and a uniformity coefficient (UC) = 1.4.

Table 1
Physical and chemical properties of the influent DSW used in this study.

Parameter	Average ± standard deviation
COD (mg L^{-1})	2798 ± 1503
SS (mg L^{-1})	874 ± 614
TN (mg L^{-1})	81.5 ± 34.1
NH_4–N (mg L^{-1})	63.9 ± 32.3
TP (mg L^{-1})	29.8 ± 14.4
DRP (mg L^{-1})	24.3 ± 16.0
pH	7.22 ± 0.71
Dry matter (%)	0.2 ± 0.1

(measured as ammonium-N (NH_4–N)) and P (measured as dissolved reactive phosphorus (DRP)) from the DSW was investigated in a batch experiment by placing varying masses of the washed, graded media in flasks (n = 3) and adding 40 mL of raw DSW to each sample. All samples were shaken for 24 h at 250 excursions per minute (epm) on a reciprocating shaker and on removal, were allowed to settle for 1 h, filtered through a 0.45 μm filter, and tested colorimetrically using a nutrient analyser (Konelab 20, Thermo Clinical Laboratories Systems, Finland). The data were then modelled using a Langmuir isotherm to establish maximum adsorption capacities (Table 2).

Table 2
Properties of the filter media used in this study.

Media type	Grading	Hydraulic conductivity of saturated media (mm s^{-1})	Maximum adsorption capacity (g kg^{-1})	
			P	N
Woodchip	10–20 mm	1.25	–	3
Sand	d_{10} = 0.2 mm; UC = 1.4	0.03	136	–

Influent samples and effluent taken from each filter column were tested for pH using a pH probe (WTW, Germany) and for suspended solids (SS) using vacuum filtration on a well-mixed subsample through Whatman GF/C (pore size 1.2 μm) filter paper. Sub-samples were filtered through 0.45 μm filters and analysed colorimetrically for DRP, NH_4–N, total oxidised nitrogen (TON) and nitrite-N (NO_2–N) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Nitrate-N was calculated by subtracting NO_2–N from TON. Unfiltered samples were tested for TP and filtered (0.45 μm) samples for total dissolved phosphorus (TDP) using acid persulphate digestion. Particulate phosphorus (PP) was calculated by subtracting TDP from TP. Unfiltered samples were tested for TN using a BioTector Analyser (BioTector Analytical Systems Ltd., Cork, Ireland) and for COD (dichromate method). Influent DSW was tested for DM content by drying at 105 °C for 24 h. All water quality parameters were tested in accordance with standard methods (APHA, 2005).

2.1. Statistical analysis

The data were analysed using independent sample t-tests in SPSS (IBM SPSS Statistics 20 Core System) with column depth, OLRs and filter media as grouping variables. The data were checked for normality and, where necessary, were log transformed to satisfy the normal distributional assumptions required. Where normality was not achieved, the non-parametric Mann Whitney *U* test was used. Probability values of $p > 0.05$ were deemed not to be significant.

3. Results and discussion

3.1. Impact of media depth

Treated effluent concentrations from the 1 m deep woodchip filters were consistently lower than those from the 0.6 m deep filters for all measured parameters at an OLR of 120 g COD m^{-2} d^{-1} (Fig. 3). However, the concentrations for COD in the final effluent (1469 ± 587 mg L^{-1} for the 0.6 m filter and 587 ± 113 mg L^{-1} for the 1 m filter) were still far in excess of the limit value for discharge to urban waters (125 mg L^{-1}; SI No 254 of 2001). The 0.6 m deep filters reduced COD, SS, TP and DRP by 46%, 54%, 7% and 5%, respectively (based on average influent and effluent concentrations), but did not reduce TN and NH_4–N concentrations to below those of the influent. Reductions of 78% COD, 95% SS, 85% TN, 82% NH_4–N, 50% TP and 54% DRP were measured for the 1 m deep filters and were consistent with those of Ruane et al. (2011), who measured reductions of 66% COD and 57% TN for 1 m deep woodchip filter pads operating at an average OLR of 173 ± 43 g COD m^{-2} d^{-1} for a 1 year period. These findings indicate that filter depth is an important consideration in the design of woodchip filters, as the 0.6 m deep filters did not provide sufficient detention time to reduce COD and SS by more than approximately 50% at an average OLR of 120 g COD m^{-2} d^{-1}. These removals were increased by a factor of approximately 1.7 when the filter depth was increased to 1 m with consequent increase in detention time.

Ammonium-N was not nitrified in any of the woodchip filters and this was most likely as a result of the high average C:N ratio (30) of the influent DSW, which was far above the optimum C:N ratio of 3–6 for nitrification (Henze et al., 2001; Eding et al., 2006). This, combined with a high OLR (120 g COD m^{-2} d^{-1}), likely resulted in the formation of a dense, non-porous heterotrophic biofilm structure, reducing the available sites for the slow growing nitrifiers (Okabe et al., 1996; Wijeyekoon et al., 2004; Nogueira et al., 2002). A nitrogen mass balance between influent and effluent carried out on the 0.6 m deep filters showed that the mass of organic nitrogen (Norg) was reduced by 23% while the mass of NH_4–N increased by 8%, with no overall TN removal. For the 1 m deep filters, the mass of Norg was reduced by 37% with a corresponding reduction in NH_4–N of 82% and an overall decrease in TN of 85%, with NH_4–N as the dominant fraction in the final effluent. Therefore, while significant TN and NH_4–N removals were achieved in the 1 m deep filters (85% and 82%, respectively), the removal processes were by physical filtration of SS and associated N (Fig. 4(A)) rather than biological transformations. Much lower SS removals were measured in the 0.6 m deep filters (Fig. 3). The average pH of the treated effluent was 7.41 ± 0.26, indicating that alkalinity was not an inhibiting factor for nitrification. Ruane et al. (2011) reported an average concentration of 22.5 mg NO_3–N L^{-1} in treated effluent from 1 m deep woodchip filter pads loaded with DSW, which had an average influent concentration of 12.9 mg NO_3–N L^{-1} and C:N ratio of 16. In the current study, there was no NO_3–N in the influent and this may have influenced the biofilm formation and consequent opportunity for development of NH_4–N oxidizers (Okabe et al., 1996).

3.2. Impact of organic loading rates

There were no significant differences in the final effluent concentrations of NH_4–N (4.1 ± 4.1; 4.6 ± 4.2 mg L^{-1}) and SS (23 ± 16; 37 ± 22 mg L^{-1}) from the 1 m deep woodchip filters operated at OLRs of 50 and 155 g COD m^{-2} d^{-1}; however, the average effluent DRP concentration (3.8 ± 1.5 mg L^{-1}) from the 50 g COD m^{-2} d^{-1} filters was significantly lower ($p < 0.001$) than from the 155 g COD m^{-2} d^{-1} filters (10.2 ± 2.9 mg L^{-1}). As the woodchip had no ability to adsorb P (Table 2), physical removal was the main mechanism for P removal. Based on the influent and effluent loading rates, 2.5 mg PP d^{-1} (318 mg PP m^{-3} d^{-1}) was retained in the 155 g COD m^{-2} d^{-1} filters, whereas 0.4 mg PP d^{-1} (51 mg PP m^{-3} d^{-1}) was retained in the 50 g COD m^{-2} d^{-1} filters.

Removals (based on the average influent and effluent load and expressed in mg d^{-1}) in the range of 71%–97% were measured for COD, SS, TN and NH_4–N, and 54%–74% for TP and DRP, were measured in both sets of filters. Final effluent concentrations of SS, NH_4–N and DRP ranged from 23 to 37 mg L^{-1}, 4.1–4.6 mg L^{-1}, and 3.8–10.4 mg L^{-1}, respectively. However, the final effluent COD concentrations from both filters (766 ± 221 mg L^{-1} for the 50 g COD m^{-2} d^{-1} filters and 604 ± 112 mg L^{-1} for the 155 g COD m^{-2} d^{-1} filters) were well above the limit values for

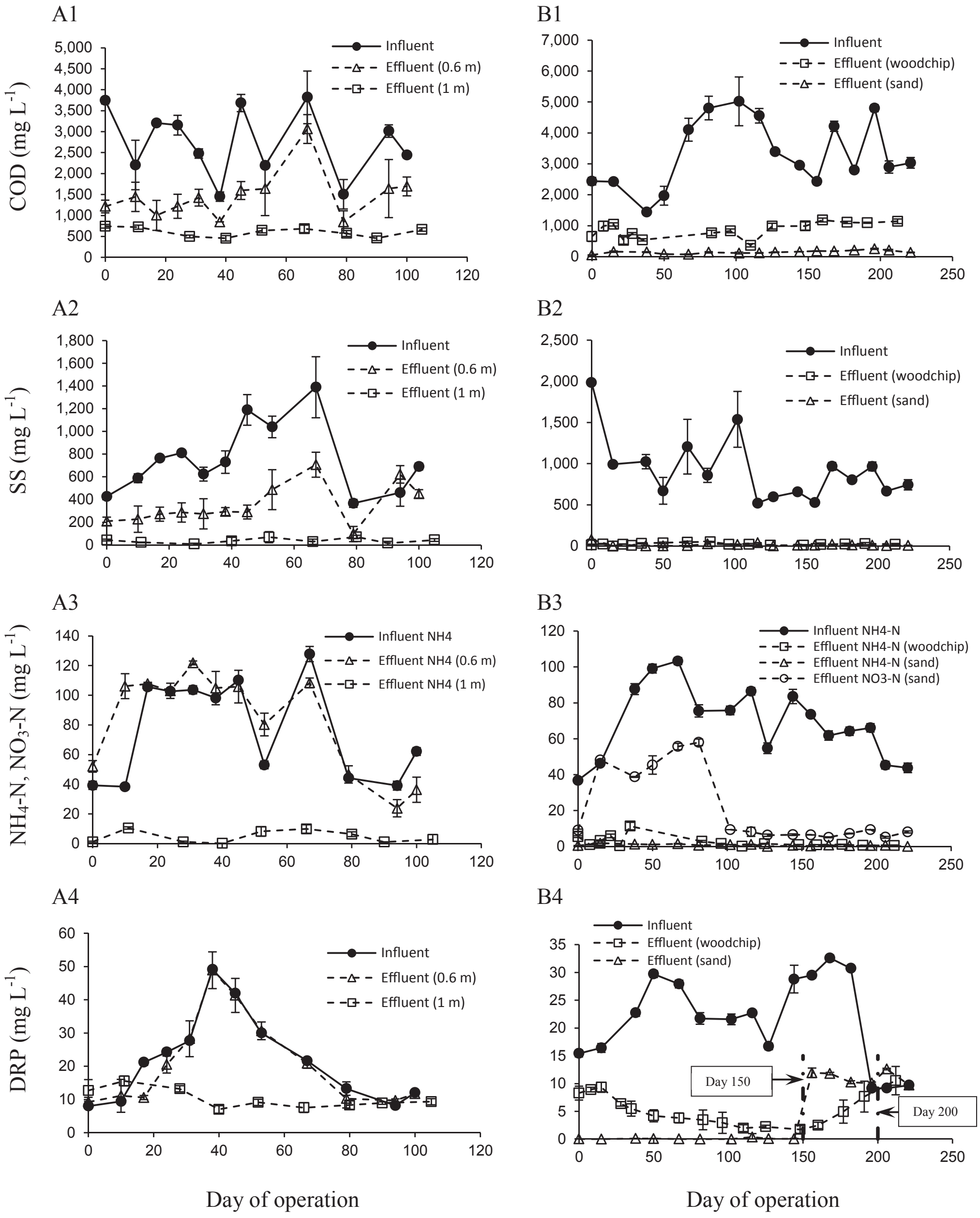

Fig. 3. Impact of media depth (A1 – A4) and media type (B1 – B4) on COD, SS, NH_4–N and DRP removals. An average organic loading rate of 120 g COD m^{-2} d^{-1} was applied to woodchip media (10–20 mm Sitka spruce) when comparing the impact of media depth (A1 – A4). An average organic loading rate of 35 g COD m^{-2} d^{-1} was applied to woodchip (10–20 mm Sitka spruce) and sand (d_{10} = 0.2 mm, UC = 1.4) media, both 1 m deep when comparing the impact of media type (B1 – B4). Error bars indicate standard deviations.

discharge to urban waters in Ireland (S.I. No 254 SI No. 31 of, 2001). Effluent mass loads for COD, SS, NH_4–N and DRP (Fig. 5) remained consistent over the duration of the study period, highlighting the capacity of the filters to effectively and consistently treat variable strength and variably loaded influent DSW.

Negligible NO_3–N concentrations were measured in the effluent, underlining the reliance on physical filtration for NH_4–N removal as illustrated by the close correlations between SS and NH_4–N mass removals for both loading rates (Fig 4(B)).

3.3. Impact of filter media

There were no significant differences between the treated effluent from 1 m deep woodchip and 1 m deep sand media (average OLR = 35 g COD m^{-2} d^{-1}) for SS (23 ± 13 and 16 ± 20 mg L^{-1}) and NH_4–N (2.9 ± 3.4 and 0.8 ± 0.5 mg L^{-1}); however, the sand outperformed the woodchip in COD removal (a final effluent of 146 ± 52 mg L^{-1} versus 873 ± 242 mg L^{-1}) and DRP removal up to day 150 (a final effluent of 0.1 ± 0.1 mg DRP L^{-1} versus 4.9 ± 2.7 mg DRP L^{-1}). The enhanced COD removals in the sand filters were reflective of their higher hydraulic retention time when compared to the woodchip filters (the hydraulic conductivity of the sand was >40 times lower than that of the woodchip (Table 2)). The enhanced DRP removals in the sand filters were as a result of their higher P adsorption capacity (136 g DRP kg^{-1}) compared with the woodchip, which had no affinity for P, and DRP reductions in the woodchip filters were associated with SS removals (Fig. 4(C)). After 150 days of operation, DRP breakthrough

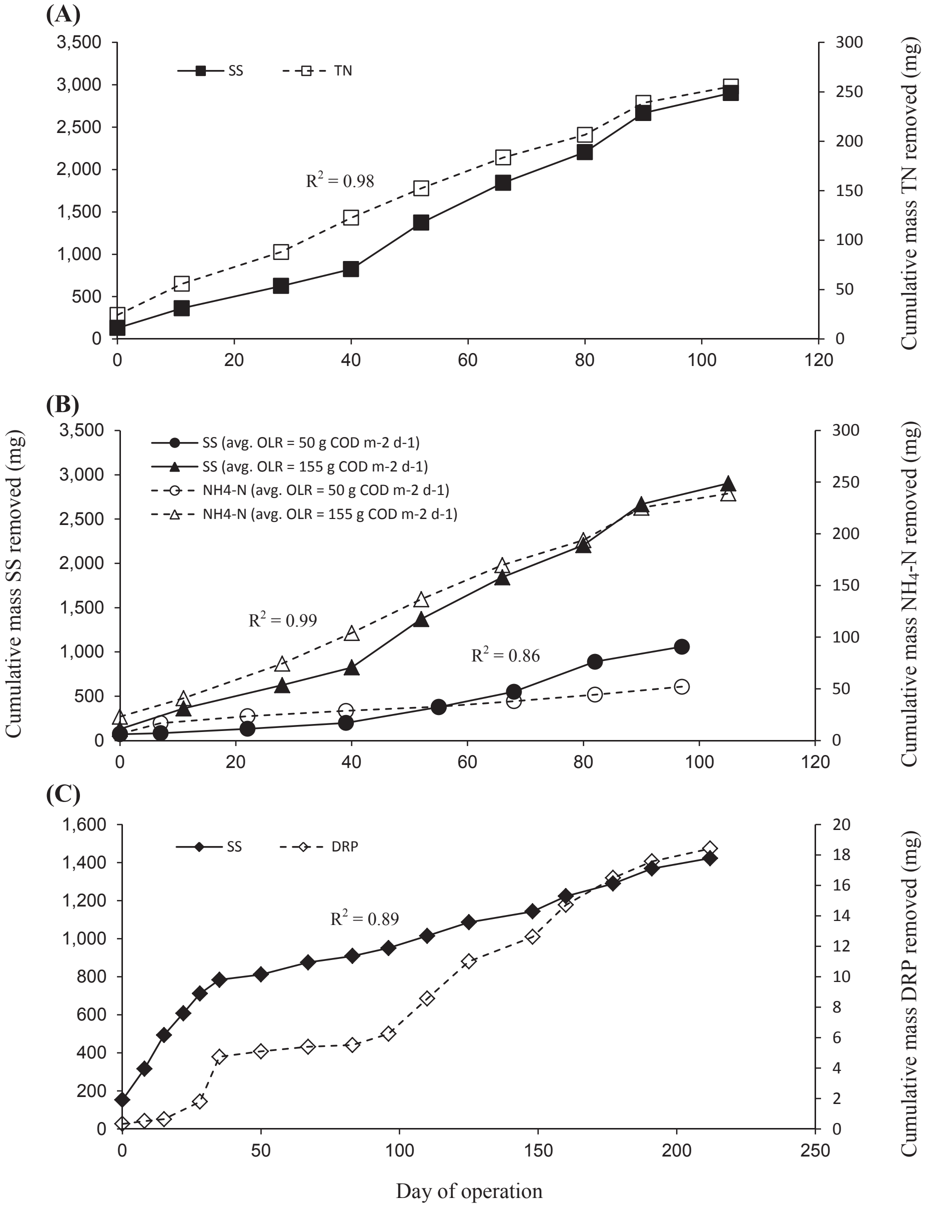

Fig. 4. Correlations between cumulative mass removals of suspended solids (SS) for1 m deep × 0.1 m Ø woodchip filters (n = 3, each set) and (A) TN loaded at 120 g COD m^{-2} d^{-1} (B) NH_4–N loaded at 50 and 155 g COD m^{-2} d^{-1} respectively and (C) DRP loaded at 35 g COD m^{-2} d^{-1}. Correlation coefficients, (R^2) indicated.

occurred quite quickly in the sand filters and at a slower rate in the woodchip filters (Fig. 3). From day 200 to the end of the study, neither the sand nor the woodchip filters removed any DRP from the influent DSW (Fig. 3). The average mass of P retained up to day 150 was 1.61 ± 1.30 and 3.89 ± 0.76 mg TP d^{-1}, 0.61 ± 0.31 and 0.96 ± 0.32 mg PP d^{-1} and 1.33 ± 0.84 and 2.58 ± 0.60 mg DRP d^{-1} for woodchip and sand filters, respectively, indicating that the sand was more effective at removing PP and also had a greater affinity for adsorption of DRP (Table 2). The mass removal rates also indicate that sand had more consistent P removal than woodchip up to day 150.

During the first 85 days of operation, nitrification occurred in the sand filters and the NO_3–N concentration rose from 0.1 ± 0.1 mg L^{-1} in the influent to 43 ± 18 mg L^{-1} in the effluent. However, the effluent NO_3–N subsequently reduced considerably, and attained an average concentration of 7.2 ± 1.6 mg L^{-1} by the end of the study (Fig. 3). The reasons for the suppressed levels of NO_3–N were possibly due to the preferential formation of heterotrophic-dominated biofilm layers limiting dissolved oxygen (DO) to the nitrifiers (Nogueira et al., 2002) as a consequence of the high influent C:N ratios in the influent wastewater (average of 38). Negligible NO_3–N concentrations were measured in the treated effluent from the woodchip filters and were always below 0.21 ± 0.19 mg L^{-1}. This indicates that even at the low OLRs used in this study, which are at the upper limit at which nitrification normally occurs in sand filters treating a similar type of wastewater (around 30 g COD m^{-2} d^{-1}; Rodgers et al., 2005), woodchip filters are unable to nitrify DSW.

3.4. Assessment of optimum filter media, configuration and operation

When assessing the suitability of the filters to treat on-farm DSW, key operating criteria must be taken into account, together

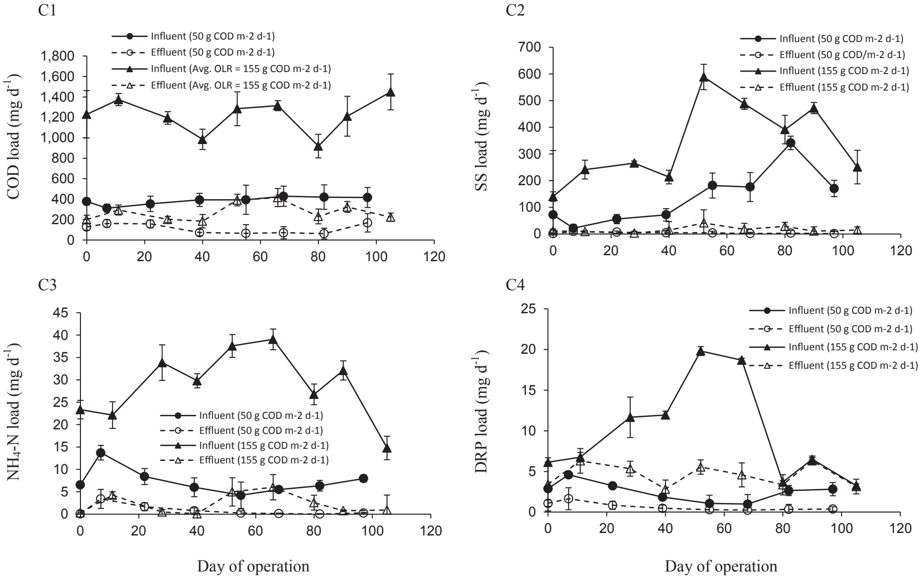

Fig. 5. Impact of organic loading rates on COD, SS, NH_4–N and DRP mass removals. The filter material used was 10–20 mm Sitka spruce woodchip, 1 m deep. Error bars indicate standard deviations.

with the main objective of reducing organic and nutrient concentrations to levels which would not adversely impact the environment if landspread. These operating criteria include items such as cost and availability of the media, robustness and longevity of performance (i.e. how well can media deal with daily and seasonal variations in flow and strength and for how long), biodegradability, and disposal of spent media.

The results of this study show that woodchip filters should have a minimum depth of 1 m to achieve required removals and can reduce the measured water quality parameters at OLRs up to at least 155 g COD m^{-2} d^{-1}. However, based on the N mass balances and effluent concentrations of NO_3–N measured in this study, the removal mechanisms in woodchip filters are primarily physical (straining) and not biological (nitrification did not occur). The suppression of biological activity may have been a function of the OLRs employed in this study, where the lowest OLR studied (35 g COD m^{-2} d^{-1}) was still at the upper limit at which nitrification normally occurs in filters (Rodgers et al., 2005).

Biological N transformations are a sustainable long-term process to reduce effluent N when compared to removal by physical straining alone. While nitrification was not observed to occur in the woodchip filters in the current study, other studies (e.g. Carney et al., 2011) have reported its occurrence for piggery wastewaters at OLRs in the range 14–128 g COD m^{-2} d^{-1}. Nitrification of DSW in sand filters has been reported in many studies (e.g. Rodgers et al., 2005; Healy et al., 2011) at OLRs in the range 20–40 g COD m^{-2} d^{-1}. Given that the composition of raw DSW normally contains very low, if any, NO_2 or NO_3 concentrations (Minogue et al., 2015), long start-up times are likely to be required to establish an active population of NH_4 oxidizers in any filter medium (Okabe et al., 1996; Lekang and Kleppe, 2000).

Surface clogging of the filter media is an operational issue that must be considered for on-farm use and while neither the sand nor the woodchip media in this study experienced surface clogging, Healy et al. (2007) reported clogging of sand filters after 42 days at an OLR of 43 g COD m^{-2} d^{-1}. In contrast, we are not aware of any reported issues with surface clogging of woodchip media, and it has been estimated that a woodchip filter may be operational for 2–3 years before surface ponding occurs (Ruane et al., 2011).

The decision to use woodchip or sand filter media is ultimately taken by synthesizing environmental benefits versus capital and operating costs. Operating costs are similar for both woodchip and sand filters (the modes of operation are identical for both), while capital costs are differentiated only by the cost of the media (filter setup for woodchip and sand are similar), which may also not differ significantly and will be location specific. Cost comparisons therefore can be made by comparing the required footprint of woodchip and sand media, both at a depth of 1 m – the minimum acceptable filter depth identified in this study. Based on the optimal OLRs identified in this study (an OLR of 155 g COD m^{-2} d^{-1} for woodchip filters, which treated the wastewater through physical processes, if not necessarily biological processes, and an OLR of 35 g COD m^{-2} d^{-1} for sand filters, which only temporarily caused the occurrence of nitrification, but clearly was at the upper OLR limit at which such filters may be operated), a filter surface area of 0.48 m^2 cow^{-1} for woodchip versus 2.1 m^2 cow^{-1} for sand would be required (Table 3). The larger area required for the sand filter combined with their lack of robustness to deal with shock loads (Healy et al., 2007) and the potential for surface clogging (Rodgers et al., 2005), indicate that woodchip filters are a better on-farm treatment option.

The optimal filter configuration identified in the current study produced a final effluent that was in excess of permissible discharge standards. For the water to be discharged to surface waters, some form of primary and tertiary treatment may be required. Primary treatment may consist of a simple sedimentation

Table 3
Comparative filter areas (per cow) of a full scale filter for optimal organic loading rates investigated in this study of 155 g COD m^{-2} d^{-1} for woodchip and 35 g COD m^{-2} d^{-1} for sand.

Q[a]	COD load[b]	Filter area per cow (m^b)	
(L d^{-1} cow^{-1})	(g COD d^{-1})	Woodchip[c]	Sand[d]
27	73.7	0.48	2.1

[a] Minogue et al., 2015.
[b] Assuming an annual average COD concentration of 2750 mg L^{-1}.
[c] Using an OLR of 155 g COD m^{-2} d^{-1}.
[d] Using an OLR of 35 g COD m^{-2} d^{-1}.

tank upstream of the woodchip filters to reduce SS in the influent DSW, and tertiary treatment might comprise the addition of downstream polishing filters using, for example, zeolite for enhanced N removal and flue gas desulphurization (FGD) gypsum for enhanced P removal. However, this would be costly for the farmer and, moreover, would mean that a discharge license may be required. Additionally, the technical and economic feasibility of using such tertiary media to act as polishing filters for DSW treatment would need to be established. Based on the results of the current study, a 1 m deep woodchip filter, with an OLR of 155 g COD m^{-2} d^{-1}, may retain up 600 mg SS d^{-1} (Fig. 5) and may reduce over 90% of the SS. Therefore, the liquid portion of the wastewater may be used in irrigation, which requires no discharge license or transport costs, and is safer (Augustenborg et al., 2008a); and, once exhausted, the spent timber residue may be incorporated into the soil (Augustenborg et al., 2008b).

4. Conclusions

On the basis of this study, woodchip filters are more effective in the treatment of DSW than sand filters. In this study, optimal performance in terms of mass of contaminants removed per day was achieved using a 1 m deep woodchip filter operated at an OLR of 155 g COD m^{-2} d^{-1}. Filtration was the dominant mechanism for N removal in the woodchip filters. The final effluent was above the concentrations at which it may be legally discharged to receiving waters. Therefore, management option employed to re-use the final effluent may be to use the liquid portion of the effluent in irrigation and, in time, to incorporate the spent timber residue into the soil.

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