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Research article

Impacts of zeolite, alum and polyaluminum chloride amendments mixed with agricultural wastes on soil column leachate, and CO_2 and CH_4 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 surface applied with unamended and chemically amended dairy and pig slurries, and dairy soiled water (DSW). The amendments to the slurries, which were applied individually and together, were: polyaluminum chloride (PAC) and zeolite for pig and dairy slurry, and liquid aluminium sulfate (alum) and zeolite for DSW. Application of pig slurry resulted in the highest total nitrogen (TN) and nitrate-nitrogen (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 (TOC) and inorganic C (TIC) 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}). 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 these losses.

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 (Liu et al., 2012; McDowell and Hamilton, 2013; Ulén et al., 2013; Fenton et al., 2017). For example, high nitrate (NO_3) concentrations in groundwater used as a drinking water source may lead to environmental (Fenton et al., 2009) as well as human health issues associated with methemoglobinemia (WHO, 2004) and cancer (Camargo and Alonso, 2006; Chiu et al., 2007). 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. Qin et al., 2010; Li et al., 2015). 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) and where crop production is increased by intensive application of fertilizers and irrigation water (Lin and Chen, 2016).

Landspreading is the most common method of slurry application (Lloyd et al., 2012) and while other 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

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soils. On the other hand, Kleinman et al. (2009) reported that incorporation of dairy manure by tillage reduced P losses in leachate because of the destruction of preferential flow pathways in the soil, while Hodgson et al. (2016) found that shallow injection of dairy slurry to grassland plots resulted in higher and more prolonged survival of faecal indicator organisms than from surface spreading. The partitioning between surface runoff and leaching from land applied agricultural slurries is determined largely by rainfall distribution and intensity, topography, and soil infiltration capacity (Aronsson et al., 2014). 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 (iv) 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 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. Jin et al., 1997; Enell et al., 2004; Dontsova et al., 2006) and while macropore structure of intact soils is disturbed during the repacking process (McLay et al., 1992), 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 polyaluminium chloride (PAC) or alum amendments, applied to dairy and pig slurries and to DSW at rates previously investigated to mitigate N, P and suspended solids (SS) losses from grassed soil in rainfall simulation studies (Murnane et al., 2015) and surface applied to repacked grassland soil columns, were also 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.

2. Materials and methods

2.1. Soil sampling and analyses

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.* 200–250 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 for ten days, 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, 1988) 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 analyzer (Konelab 20, Thermo Clinical Laboratories Systems, Finland).

2.2. Soil batch studies

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 wastewater 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 analyzer (Konelab 20, Thermo Clinical Labsystems, Finland). The data were then modelled using a Langmuir isotherm to establish the maximum soil P-adsorption capacity.

2.3. 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 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 0.1 M 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).

2.4. Slurry amendments

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