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Development of a novel biofilter cover to offset methane emissions from dairy effluent ponds

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Prepared for Dr Gerald Rys, Ministry for Primary Industries
by Chris Pratt, Kevin Tate and Julie Deslippe, Landcare Research
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Summary

Biofiltration, through which CH_4 is oxidised by methanotrophic bacteria, is a potentially effective strategy for mitigating CH_4 emissions from anaerobic dairy effluent lagoons/ponds, which typically do not produce enough biogas for energy recovery. This study reports on the effectiveness of a biofilter cover design for oxidising CH_4 produced by dairy effluent ponds. The biofilter cover was tested under laboratory and field conditions. In the laboratory experiments, a volcanic pumice soil, garden-waste compost and a mixture of these two materials were tested as biofilter media (5 cm thickness) suspended above simulated dairy effluent ponds. Methane fluxes delivered to the filters were similar to emission rates from typical dairy effluent ponds. All materials oxidised more than 95% of the CH_4 influx (13.9 g CH_4 m^3 h^{-1}) after 2 months, and continued to display high oxidation rates for the remaining 1 month of the trial. The volcanic soil biofilters exhibited the highest oxidation rates (99% removal). When the CH_4 flux was doubled for a month, CH_4 removal rates remained >90% for all soils (maximum = 98%, for the volcanic soil). Nitrous oxide emissions from the soils were negligible (maximum = 19.9 mg N_2O m^3 h^{-1}) compared with CH_4 oxidation rates. This was particularly evident from the volcanic soil which had a much lower microbial-N (75 mg kg^{-1}) content than the compost-based filter soils (>240 mg kg^{-1}). The sustained and effective CH_4 oxidation rates observed in this study indicate that a biofilter cover based on this design could potentially mitigate most of the CH_4 emissions from typical dairy effluent ponds. The design was also tested at field-scale, and involved a 2m x 2m biofilter (5 cm thickness) receiving biogas emissions from a dairy effluent pond at Massey University. The filter comprised garden-waste compost and was set-up on the bank of the pond. Biogas from the pond surface was directed through the filter and the system was periodically sealed to measure gas fluxes. The field filter achieved a maximum CH_4 oxidation efficiency of 18 g m^{-3} h^{-1}. Nitrous oxide production from the field filter was negligible (< 0.3% of the CH_4 emissions offset). The promising result of this filter design warrants further field-testing. Landcare Research is currently planning this work which, will allow the efficiency of a biofilter actually floating on top of an effluent pond to be assessed.

1 Introduction

Lagoons or ponds are used on dairy farms around the world to store effluent washdown from milking sheds (Safley & Westerman 1992; Cronk 1996; Craggs et al. 2008). These ponds are a significant source of methane (CH_4), a potent greenhouse gas (GHG) with a global warming potential at least 21 times greater than that of CO_2 (Shindell et al. 2009). For farms with large herd sizes, the CH_4 produced from effluent ponds could be captured and used as an energy source (NIWA 2010). However, most New Zealand dairy farms have about 450 cows, so they are too small to make this option economically viable. As farmers have no incentive to mitigate their GHG emissions, CH_4 generated from effluent ponds is left to escape to the atmosphere. Although the inclusion of agriculture into the Emissions Trading Scheme (ETS) was recently deferred until after 2015, farmers will eventually need practical and cost-effective options to mitigate their effluent CH_4 emissions.

For most dairy farms, biofiltration offers a practical and potentially cost-effective technology to reduce their dairy effluent pond CH_4 emissions. Methane biofilters contain an active population of methanotrophs. These are aerobic bacteria that oxidise CH_4 and convert it to water vapour, biomass and CO_2 (with a GWP of 1 compared to at least 21for CH_4). Methane biofilters have been widely studied for their application to reduce landfill CH_4 emissions (e.g., Park et al. 2002; Haubrichs & Widmann 2006), but very little published information exists on their potential to mitigate agricultural emissions. Previous studies by the authors (Tate et al. 2012; Pratt et al. 2012a) documented the potential to use methanotrophs in a CH_4 biofilter, and demonstrated the successful performance of a soil biofilter treating CH_4 emissions from a section of a dairy effluent pond. The filter showed high CH_4 oxidation rates (up to 16 g CH_4 m^3 h^{-1}) over 16 months without any maintenance. However, this initial filter design was cumbersome and consisted of a gas recovery system on the pond's surface, gas transfer pipes, and an enclosed biofilter unit on the nearby bank of the pond. A fan was also required to provide air to maintain aerobic conditions for the methanotrophs. At full-scale, this design would be very expensive and would not offer any real cost or performance advantage over a thermal combustion system. However, we have now overcome these disadvantages by designing a shallow biofilter that sits atop an effluent pond, either by floatation or suspension. This new design does not need a gas recovery and transfer system. There is also no need for a fan or pump because the methanotrophs can obtain oxygen by passive diffusion of air. If a floating biofilter can be successfully developed to treat dairy effluent pond emissions, this would provide a novel and cost-effective solution for farmers to reduce their CH_4 emissions.

2 Objectives

Our aim in this study was to test the effectiveness of an improved design of biofilter where the filter is an integral part of a pond cover to oxidise CH_4 emissions from dairy effluent ponds. The cover design was tested in both the laboratory and on a dairy farm effluent pond at Massey University. This project extends our earlier research reported in a previous MAF/MPI report entitled: Development of novel technologies to reduce agricultural methane emissions, Contract: C09X0806 (Walcroft et al. 2011).

3 Materials and Methods

3.1 Laboratory cover filter experiments

3.1.1 Soil collection and preparation

Two soil types were used as biofilter medium in the laboratory experiments. The first was volcanic pumice collected from a landfill cover in Taupo. Soils from this area are classed as pumice (Andisols) derived from volcanic activity approximately 2000 years ago (Beets et al. 2002). The second soil was 6-month-old compost from a green-waste-processing site in Palmerston North. The volcanic soil had exhibited high CH_4 oxidation rates in previous column experiments (Tate et al. 2012; Pratt et al. 2012b), while the compost showed high CH_4 uptake rates in batch tests conducted before carrying out this research. The soils were sieved to <5 mm to remove coarse materials and then moistened to approximately 60% of their water-holding capacity, which is in the ideal range for optimal CH_4 oxidation (Humer & Lechner 1999).

3.1.2 Biofilter cover experiments

Nine small-scale simulated dairy effluent ponds were set-up in the laboratory, and were constructed using 50 L clear plastic containers. Each "pond" was filled to 5 cm depth with water, and an artificial biogas (20% CO_2: 80% CH_4) was bubbled through the water layer from a gas cylinder. Using rotameters the CH_4 flow rate in each container was set at a level similar to a typical CH_4 emission rate (i.e. 26 L m^{-2} d^{-1}) reported for dairy effluent ponds by Craggs et al. (2008). The laboratory temperature was not controlled but it was monitored and logged half hourly over the course of the experiment. The average temperature during the experiment was 25^{o}C (maximum 29^{o}C, minimum 19^{o}C).

The containers were sealed and air was delivered through the top of each unit at 115 ml min^{-1} using a rotameter. The lids were fitted with an outlet vent with a small diameter (4 mm) to allow the escape of gases and, at the same time, maintain an equilibrium gas mixture of air and biogas in the containers. Before any soils were placed into the containers, gas flow rates were verified on two occasions.by measuring CH_4 concentrations in the gas exiting the containers. Because the biogas and air flow rates entering the units were quantified, the theoretical CH_4 value exiting the containers could be calculated. The average deviation from the theoretical value was 4.6 % (maximum 12%, minimum 0.2 %), so the readings on each rotameter were considered to be accurate within 5%.

Biofilter covers for the simulated effluent "ponds" were created by suspending the soils (described above) on a stainless steel mesh above the water level in each container. The aperture size of the mesh was 2 mm, which was chosen to prevent soil falling into the water. The soil thickness in the containers was loosely packed to a depth of 5 cm, which gave a total filter volume of 8 L. Three replicates of the compost soil; volcanic pumice soil; and a 50:50 (by volume) mixture of compost and pumice were placed into the nine containers. The experimental set-up is shown in Figure 1.

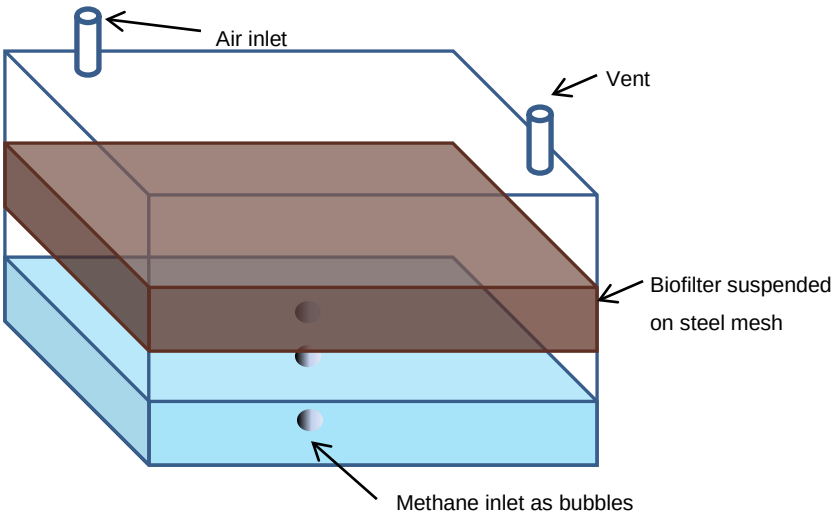

Figure 1: Schematic representation of the biofilter units

This first phase of the experiment ran for 3 months. Subsequently, the CH4 concentration delivered to the filters was doubled to assess how the filters might perform on effluent ponds that have higher than average CH_4 emission rates. The trial was conducted for 4 weeks.

Gas samples were collected on average three times per week from the filters' vents and twice from the space between the soil layer and the water level (in order to confirm that sufficient oxygen was being delivered to the base of the soil layers). Gas samples were obtained manually using 10–ml syringes.

3.1.3 Biofilter soil sampling details

During the experiment, the soils in the filters were sampled on four occasions (after one month; two months; three months; and at the end after the CH_4 concentration was doubled) for physicochemical analysis. A square grid system, comprising 3 × 5 cells, covering the filter surface was devised for choosing sampling locations within each filter. For each sampling event, three replicate 100–ml soil cores were collected from each filter using a random number generator to select positions on the sampling grid. The cores were backfilled with fresh soil and all sampled locations were exempt from future sampling.

3.1.4 Biofilter soil physiochemical analyses

Three replicate batches of each of the original soils (i.e. before they were put into the filter containers) were analysed for their pH, available (Olsen)-P, total C, total N, ammonium (NH_4^+)-N, nitrate (NO_3^-)-N, microbial biomass N and C, water holding capacity and moisture content, as these parameters have all been shown to regulate biological CH_4 oxidation (Hanson & Hanson 1996). The above analyses were also carried out on samples collected after 3 months of the experiment, and after doubling the inlet CH_4 concentration. For samples collected during the other periods (i.e. after 1 month and 2 months), only ammonium (NH_4^+)-N, nitrate (NO_3^-)-N, available-P and microbial biomass N and C analyses were performed, as these were the key parameters considered prone to the greatest degree of fluctuation during the experiment.

Moisture was determined by drying the samples for 24 h at 105˚C. Water-holding capacity was measured by keeping a portion of soil overnight with water (1:2 ratio) in a capped filter funnel, removing the cap the following day, letting the soil drain for 3 hours and then measuring the moisture content of the saturated soil pH was measured in a 1:2.5 water suspension (Blakemore et al. 1987). Total C and N were measured by combustion in a FF-2000 CNS analyser (LECO Corporation, St. Joseph, MI, ISA). Olsen-P was determined by extraction with bicarbonate (0.5M sodium bicarbonate, pH 8.5, 1:20 soil:extractant, 30 minutes shaking), and phosphorus concentrations measured in the extracts by the ascorbic acid/ammonium molybdate/ antimony potassium tartrate colorimetric method on a Lachat FIA 8000. Nitrate-N and NH_4^+-N were extracted using 2M KCl (1:10 soil:extractant, 1 hour shaking), and measured colorimetrically on a Lachat QuickChem FIA 8000. Microbial biomass C and N were determined following the methods of Vance et al. (1997). Unless otherwise stated, data are expressed on an oven-dry (105˚C) weight basis. The particle density, dry and wet bulk density, and porosity of the soils were calculated following the techniques described by Gradwell (1972).

3.2 Field cover filter experiment

A field-scale 'cover' filter was constructed on a research dairy farm at Massey University in the Manawatu. The filter was constructed on the bank of the farm's effluent pond using a 2 m × 2 m stainless steel container. The base of the container was filled with water to simulate a pond and this water layer was overlain by porous steel mesh. Compost soil collected from the green waste site in Palmerston North was placed on the mesh at a uniform thickness of 5 cm (same as for lab experiments), and this corresponded to a total volume of 200 L of soil. The compost soil was chosen because it was the best performing soil in the laboratory experiments at the commencement of the field experiment.

Biogas captured by a 2 m × 2 m plastic cover floating on the pond's surface was piped into a volumetric flow meter. From the flow meter, the biogas was pumped into a ring-shaped diffuser in the water layer of the biofilter unit so that the gas bubbled up through the water and into the soil layer above. This method was seen as the best way to simulate a cover biofilter overlying the pond's surface, and by having the unit on the pond's bank, the design allowed for the filter to be sealed periodically to measure gas fluxes. Biogas flow rates recorded at the beginning of the trial indicated that the Massey University pond produced much higher CH_4 emissions than expected from a typical NZ dairy effluent pond (by a factor of approximately 10, according to results from Craggs et al. 2008). This high emission rate was likely because the pond is on a research farm, and periodically receives milk dumped from vaccine trials, as well as other organic materials such as newly tested feed residues (pers. comm. farm manager). Accordingly, in this experiment the biogas fed into the biofilter from the pond cover was first reduced by approximately 80% using a solenoid valve. This resulted in a CH_4 influx through the filter of approximately double the emission rate for a typical pond (Craggs et al. 2008). We considered this would be reasonable for assessing CH_4 flows from particularly productive dairy effluent ponds.

The soil layer in the biofilter received oxygen from passive diffusion of air. However, when sampling was conducted, a lid was placed over the filter unit and air then had to be pumped into the headspace above the soil at a controlled rate to maintain the active methanotroph population. By knowing the air flow rate and the biogas flow rate, CH_4 oxidation rates could then be determined by measuring CH_4 concentrations entering and exiting the unit. Gas samples were collected using a syringe, and samples were collected in duplicate approximately every month. Moisture and temperature probes were placed in the soil layer in

the biofilter and these parameters were logged and recorded half-hourly. The experiment was monitored for nearly 8 months.

3.3 Gas analyses

Methane, CO_2 and N_2O concentrations in gas samples were measured by gas chromatography (Varian CP-3800) using a flame ionisation detector (FID), thermal conductivity detector (TCD) and electron capture detector (ECD), respectively. Oxygen concentrations in the gas samples were measured by a hand-held probe (Apogee, Model 201).

4 Results and Discussion

4.1 Laboratory cover filter experiments

4.1.1 Biofilter performance

Results (Fig. 2) show that all soil biofilters were effective at oxidising CH_4 throughout the entire experiment. For the first phase of the experiment, when the CH_4 influx was similar to a typical dairy effluent pond emission rate (Fig. 2a), the volcanic soil filters' mean CH_4 removal rates steadily increased to 13.7 g m^{-3} h^{-1} (99% removal, Fig. 2a). The filters comprising compost soil and the compost/volcanic soil mixture initially displayed high oxidation rates (mean above 12 g CH_4 m^{-3} h^{-1}), but then experienced rapidly diminishing oxidation rates for a few days (mean down to about 5 g CH_4 m^3 h^{-1}), before their CH_4 oxidation rates again increased (mean = 13.6 g CH_4 m^{-3} h^{-1} by the end of this phase of the experiment, Fig 2a).

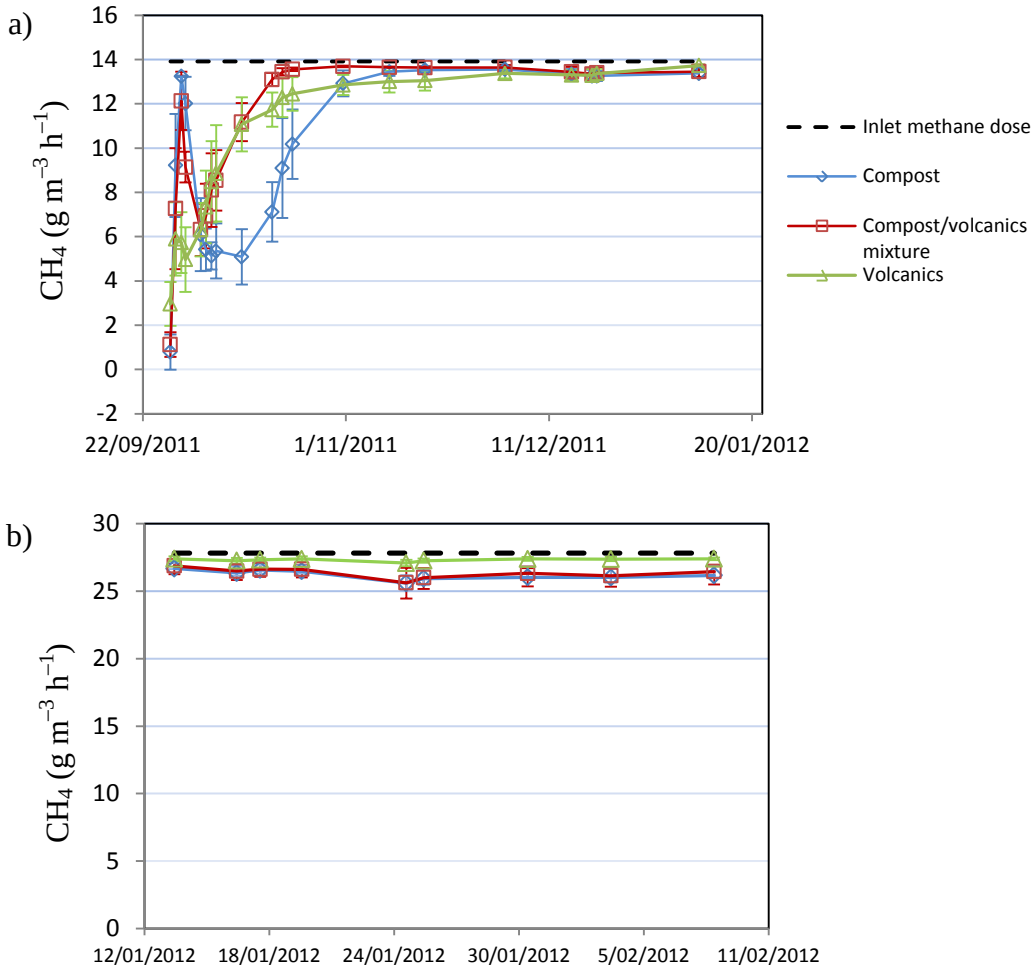

Figure 2: Methane oxidation rates by the biofiltermaterials treating CH_4 influxes: a) commensurate with typical dairy effluent pond emission rates (from Craggs et al. 2008); and b) double typical pond emission rates. Mean values of 3 replicate filters comprising each soil type are shown, with standard deviation.

In the second phase of the experiment, when the CH_4 influx was doubled, all filters continued to show high CH_4 oxidation rates (Fig. 2b). The volcanic soil filters exhibited the highest CH_4 oxidation rates under this increased influx (mean = 27.3 g CH_4 m^{-3} h^{-1}, 98.2% removal efficiency), while the mean oxidation rate of the compost and the compost/volcanic soil filters was 26.2 g CH_4 m^{-3} h^{-1} (94.2% removal) and 26.4 g CH_4 m^{-3} h^{-1} (94.7% removal), respectively. Oxygen concentrations in the air space between the suspended soil filters and the water surface were always above 13%v while CH_4 concentrations were <0.4% ppmv (data not shown). Hence, O_2:CH_4 ratios were consistently above the 2:1 ratio necessary to complete the stoichiometric conversion of CH_4 to CO_2 throughout the soil profiles in each filter (i.e. the supply of O_2 to the methanotrophs was not restricted).

The CH_4 oxidation rates by the compost and volcanic soils when the inlet CH_4 flux was doubled were 70 and 60 µg CH_4 g^{-1} h^{-1}, respectively. By comparison, Scheutz et al. (2009) reported much lower removal rates for methanotroph-rich soils; between <1 and 40 µg CH_4 g^{-1} h^{-1}. Although it can be misleading to compare CH_4 oxidation rates between different studies, due to variation in experimental design, the soils assessed in this study clearly exhibited very high CH_4 removal compared with literature values. The high oxidation rates

by the soils assessed in this study can be partly attributed to their physical properties (Table 1).

Table 1: Physical properties of biofilter materials

Soil type	Water holding capacity (% dry wt)	Dry bulk density (kg m^{-3})	Porosity (%)
Compost	197	390	83
Volcanic	84	545	77
Compost/volcanic mixture	120	468	80

The porosities of the compost and volcanic soils were exceptionally high while their bulk densities were low (Table 1) compared with literature values for other biofilter soils (porosity is generally about 40% and bulk density is approximately 1 kg l^{-1}: Kightley et al. 1995; Humer & Lechner 1999; Kettunen et al. 2006). High porosity and low bulk density were shown to be favourable physical properties for CH_4 oxidation by various types of volcanic soils in earlier studies by the authors (Tate et al. 2012; Pratt et al. 2012b).

In addition to physical soil parameters, several chemical factors, such as pH, organic C, N and P, have been reported key drivers of high methanotroph activity (Hanson & Hanson 1996; Nikiema et al. 2007). These parameters were monitored in the soil filters over the duration of the experiment and the results are shown in Table 2. Moisture levels consistently decreased in all soil biofilters during the experiment, yet did not reach levels considered suboptimal for CH_4 oxidation (<25% wt/dry wt; Nikiema et al. 2007). In the volcanic and compost soil filters, moisture decreases became exponentially smaller over each sampling period. Given such active CH_4 oxidation rates occurring in each of the biofilters it is unlikely that soil moisture levels will ever decrease to suboptimal levels in real filter systems, as water is produced during CH_4 oxidation. Olsen-P levels also diminished in the biofilter soils over time, but this did not necessarily mean that P was increasingly unavailable to methanotrophs. Rather, decreasing Olsen-P most likely reflected incorporation of P into the soil microbial pool. Attempts to measure microbial biomass P in the soils were unsuccessful as the soils' have very high P sorption capacities.

Soil pH also decreased in the soil biofilters with time. In field-scale biofilters pH reduction is likely to be even more pronounced than in this study because biogas from dairy effluent ponds contains acid-forming gases such as hydrogen sulphide. Given the importance of stable pH levels for optimal methanotroph activity (Nikiema et al. 2007), it will be occasionally be necessary to monitor pH levels in field biofilters.

Table 2: Chemical parameters and moisture contents of biofilter materials. Mean values shown for each data point are from 9 replicates (i.e. 3 replicates within each filter, 3 filters of each soil type), with standard deviation values in brackets

Biofilter soil type	Sample interval	pH	Moisture (wt %)	Organic C (%)	Total N (%)	NO_3-N (mg kg^{-1})	NH_4+N (mg kg^{-1})	Olsen-P (mg kg^{-1})	Micro-biomass-C (mg kg^{-1})	Micro-biomass-N (mg kg^{-1})
Compost	Start	8.02 (0.04)	130 (4.7)	18.03 (1.8)	1.13 (0.07)	183 (13.5)	2.4 (0.06)	401 (9.1)	2340 (859)	417 (81)
	1 mo	NM	111 (6.3)	NM	NM	1.5 (0.64)	5.4 (0.73)	337 (12.1)	2617 (414)	567 (31)
	2 mo	NM	100 (16.4)	NM	NM	0.1 (0.12)	1.9 (0.98)	265 (23.3)	3731 (689)	514 (62)
*end of testing average CH_4 emission rate from ponds	3 mo	7.95 (0.09)	83 (22)	18 (1.2)	1.29 (0.07)	0.3 (0.12)	1.1 (2.45)	247 (21.6)	3744 (1271)	551 (89)
*end of testing high CH_4 dosing rate	4 mo	7.45 (0.16)	81 (24.6)	17.3 (1)	1.25 (0.04)	0.8 (1.4)	6.7 (7.2)	230 (19.8)	5190 (1658)	588 (87)
Volcanic	Start	6.21 (0.04)	66 (0.58)	3.49 (0.15)	0.27 (0.01)	24 (0.23)	1.4 (0.15)	14 (0.58)	333 (100)	75 (6)
	1 mo	NM	57 (5.0)	NM	NM	0.1 (0.05)	3.3 (3.6)	12 (0.3)	997 (147)	116 (8.8)
	2 mo	NM	51 (3.2)	NM	NM	0.3 (0.24)	<0.1	10 (1.1)	1387 (77)	133 (8.3)
**end of testing average CH_4 emission rate from ponds*	3 mo	6.52 (0.16)	47 (10.2)	4.32 (0.33)	0.33 (0.01)	0.4 (0.09)	0.5 (1.28)	9 (0.39)	1356 (245)	162 (10.4)
**end of testing high CH_4 dosing rate*	4 mo	5.89 (0.27)	48.8 (17.5)	4.15 (0.49)	0.33 (0.02)	0.6 (0.58)	2.5 (2.59)	7 (0.81)	1780 (412)	177 (15)
Compost/ volcanic mixture	Start	7.69 (0.03)	98 (2.7)	10.76 (0.98)	0.70 (0.04)	104 (6.9)	1.9 (0.11)	208 (4.8)	1337 (479)	246 (44)
	1 mo	NM	71 (1.7)	NM	NM	2.5 (4.0)	3.3 (0.43)	109 (8.7)	1753 (323)	310 (36)
	2 mo	NM	70 (6.9)	NM	NM	1.4 (1.8)	0.9 (0.55)	104 (6.9)	2404 (382)	253 (34)
**end of testing average CH_4 emission rate from ponds*	3 mo	7.50 (0.12)	56 (16)	8.53 (0.67)	0.65 (0.04)	0.7 (0.3)	2.3 (4.27)	95 (14.2)	2400 (774)	362 (57)
**end of testing high CH_4 dosing rate*	4 mo	7.10 (0.2)	43.8 (14.1)	8.56 (0.8)	0.65 (0.06)	0.5 (0.35)	2.8 (1.72)	77 (18.8)	3087 (714)	349 (68)

Microbial biomass C concentrations increased in all filter soils during the experiment, indicating the production of new biomass by the methanotroph communities in the biofilters. The organic C content of the volcanic soil filters showed a net increase by the end of the trial. The carbon in the CO_2 emitted from the volcanic soil biofilters was balanced by the amount of organic C accumulated (9 g C L) in the soil. By contrast, organic C levels decreased in the compost and compost/volcanic soil mixtures, indicating that the high stocks of readily available C were being respired by the biological community faster than carbon-immobilisation by the methanotrophs in these compost-based systems. The results indicate that while methanotrophs can obtain their carbon requirements from CH_4 oxidation, depending on the materials used in the biofilter, monitoring of organic C levels in biofilters may be needed to ensure that C loss from respiration does not exceed C fixation.

Ammonium-N concentrations fluctuated and NO_3^--N decreased in the soil biofilters throughout the experiment. However, microbial biomass N levels increased in the soils, indicating that the methanotrophs were not N-limited at any stage of the experiment. In fact, the increased total N contents of the compost and volcanic soil filters suggest that the soil microbial communities were capable of fixing N from the atmosphere. Overall, the trends in physicochemical parameters in the biofilter soils indicate a self-sustaining methanotroph community capable of achieving efficient CH_4 oxidation rates over a prolonged period (4 months).

4.1.2 N_2O emissions

Nitrous oxide fluxes from the biofilters were monitored because N_2O has a global warming potential about 14 times greater than CH_4 (Melse & Van Der Werf 2005). Consequently, the production of N_2O in biofilters has the potential to compromise the efficacy of the technology. Figure 3 shows that over the course of the experiment N_2O fluxes were highly variable between the compost, compost/volcanic mixture and volcanic soil biofilters.

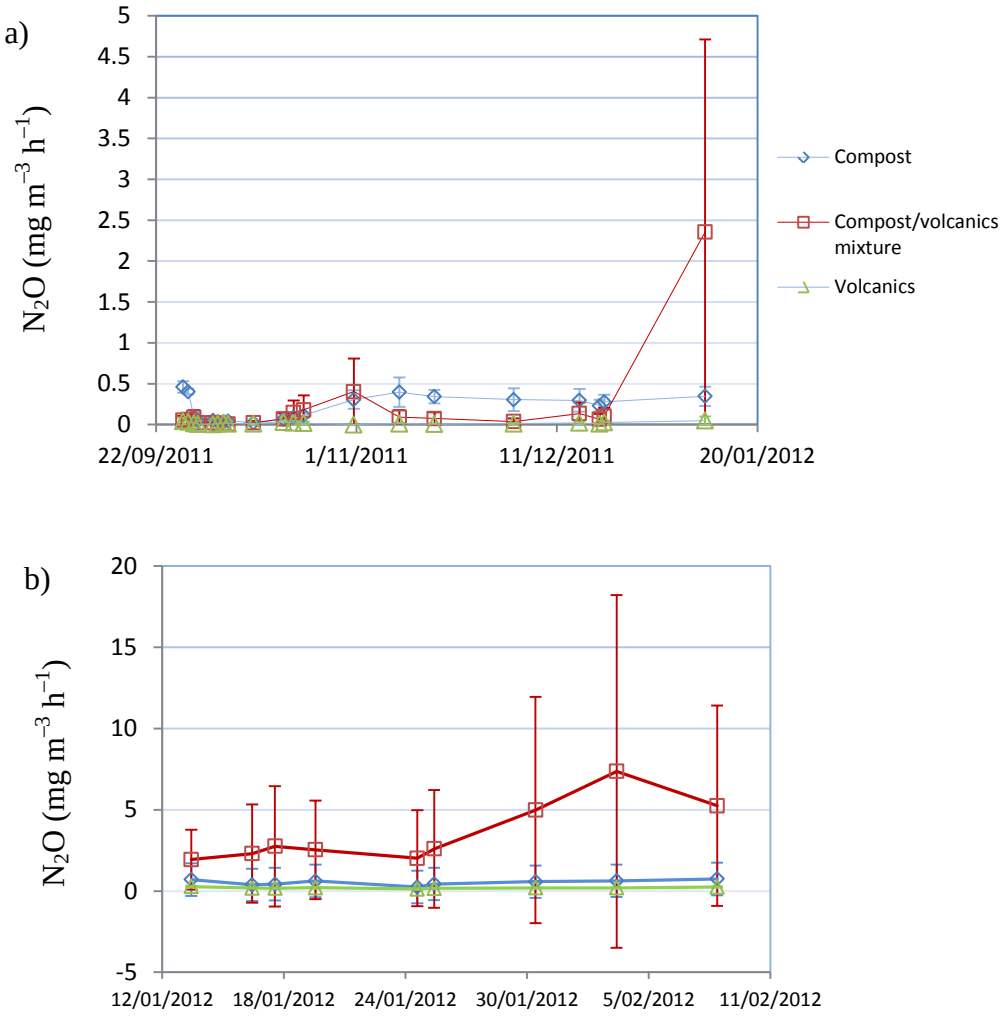

Figure 3: Nitrous oxide production rates by the different materials treating various CH_4 inlet doses a) matching typical emission rates from dairy effluent ponds (from Craggs et al. 2008); b) twice the emission rate of typical ponds. Mean values of 3 replicate filters comprising each soil type are shown, with standard deviation.

The compost and compost/volcanic soil mixture filters produced more N_2O than the volcanic soil filters (Fig. 3a and 3b) probably because there were higher total N and microbial biomass N concentrations in the compost compared with the volcanic soil (Table 2). Towards the latter stages of the experiment, the compost/volcanic mixture clearly produced the greatest N_2O fluxes. One of these filters in particular, produced much higher N_2O emissions than the others (up to 19.9 mg N_2O m^3 h^{-1}), highlighting the fact that soil microcosms can be extremely heterogeneous and that microbial processes can diverge very quickly even between two soils of the same origin.

The N_2O production observed was probably by nitrification as the filters were kept aerobic throughout the experiments. There were, however, no obvious correlations between N_2O spikes and any of the soil physicochemical parameters that were monitored. Nonetheless, the results in Figure 3 clearly show that soils with high microbial-N levels are more susceptible to N_2O production within engineered biofilters. The main focus on N_2O emissions in this

study was on the global warming potential of this gas. Comparison of data between Figures 2 and 3 shows that the quantities of N_2O produced from each filter were much lower than the quantities of CH_4 oxidised. Even factoring in the high GWP of N_2O (14 times that of CH_4), the maximum N_2O emission was still only 280 mg CH_4-equivalents m^3 h^{-1} for one of the compost/volcanic soil mixture filters. This value corresponds to only 1% of the quantity of CH_4 oxidised by that particular filter. Therefore, the impact of N_2O production from the biofilters seems negligible compared with the CH_4 oxidation rates. Nonetheless, any production of N_2O from biofilters is undesirable because of its potency compared with CO_2 and CH_4. Moreover, constant monitoring of N_2O emissions from biofilters containing compost is recommended, based on the sudden spike in N_2O emissions observed from the compost-based filters in this study.

4.2 Field cover filter experiment

The performance of the field cover filter is shown in Figure 4. From the beginning of the experiment in August 2011, through spring and into the summer months, the CH_4 oxidation efficiency of the filter increased from approximately 10 g m^{-3} h^{-1} to 18 g m^{-3} h^{-1}, representing a removal efficiency of almost 50% of the inlet flux. From February through to April 2012, the biogas cover was removed from the pond in order to accommodate pond drainage works and to repair damaged temperature sensors within the cover. When the cover was replaced on the pond, the biogas emission rate from the pond had decreased, as had the CH_4 oxidation efficiency of the filter, to about 3 g m^{-3} h^{-1} (Fig. 4).

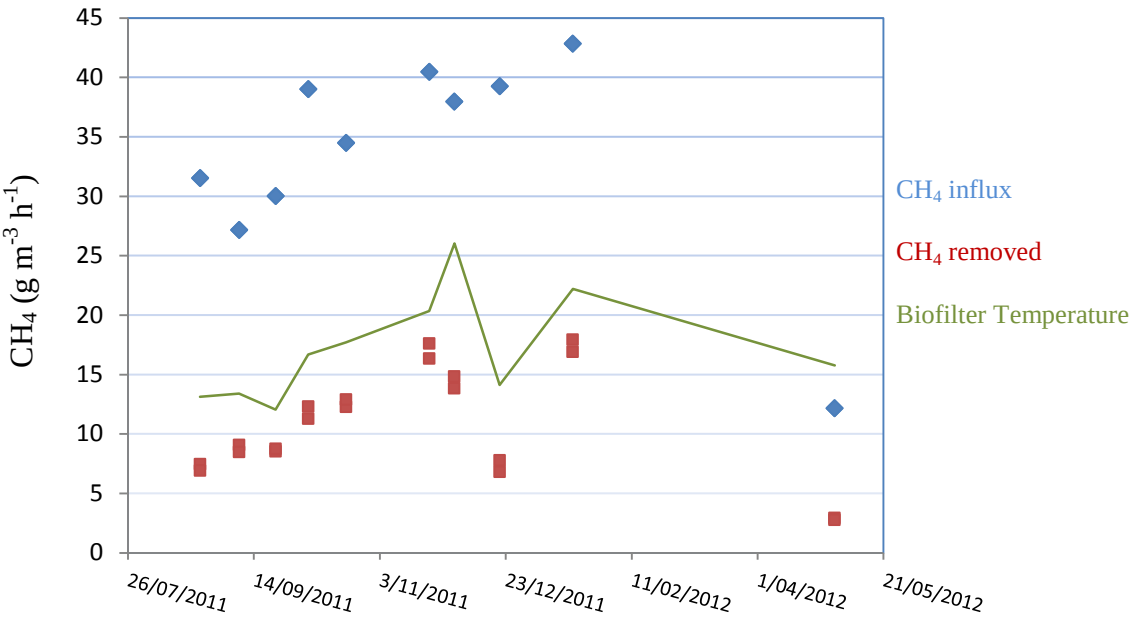

Figure 4: Methane oxidation rates by the field cover filter. Each measurement is shown, including duplicate samples collected during each sampling interval.

The efficiency of the field filter (max oxidation rate = 18 g CH_4 m^3 h^{-1}) wasn't as high as for the lab-scale filters (max oxidation rate = 27 g CH_4 m^3 h^{-1}). One factor accounting for this difference was undoubtedly the temperature differences between the lab (average = 25°C) and field (variable, from 0 to 30°C) experiments. Methane oxidation was strongly related to biofilter temperature in the field experiment (R^2 = 0.54). Certainly, oxidation rates diminish during the colder winter months, as observed in a previous early prototype biofilter treating

effluent pond emissions (Pratt et al. 2012a). However, data from that study (Pratt et al. 2012a) also showed that only 8–10% of total CH_4 emissions from dairy effluent ponds occur during winter months (June–August for NZ). Thus, diminished winter activity is apparently not a critical issue influencing the overall performance of biofilters treating effluent pond CH_4 emissions.

The lower CH_4 oxidation rates by the field compared with the lab filter could also be influenced by the erratic delivery of pulses of CH_4 to the field filter. These pulses occurred because a large proportion of the CH_4 produced under the pond cover had to be diverted from the filter (which was necessary to avoid delivering unrepresentatively high CH_4 emissions to the filter: refer to Methods section for discussion on this additional factor). These erratic pulses of CH_4 fed through the filter may have affected the responses of the methanotrophs in the compost soil, as they may have periodically been effectively starved of CH_4 for extended periods, followed by high fluxes. This type of pulsing should not be a problem for biofilters overlying dairy effluent ponds, as CH_4 is continually delivered to the pond's surface and then to the biofilter cover from methanogens degrading the sludge at the bottom of the pond.

Furthermore, the lab-scale experiments revealed that the volcanic soil was actually more effective at CH_4 oxidation than the compost soil over the long-term (> 3 months). This was not the case at the start of the lab trials, which was the reason the compost soil was selected for the field filter. The better long-term performance of the volcanic soil is perhaps not surprising, given it provides ideal conditions for supporting an active methanotroph population such as a strong water retention capacity, good aeration and high surface area. For future field trials, we favour using the volcanic pumice soil as the biofilter medium rather than organic-based materials, although we plan to test other artificial materials, such as perlite.

4.3 Future considerations

Overall, CH_4 oxidation rates achieved by the lab-scale biofilters were exceptionally high and self-sustaining. As expected, the oxidation rates by the field system were lower than those observed in the lab filters, as the latter were tested under ideal laboratory conditions. Nonetheless, the field filter produced promising results that warrant a new approach to field-testing by examining how biofilters perform when they are placed over the top of effluent pond surfaces. It will be a challenge to measure gas fluxes in such systems, but planning is underway at Landcare Research to determine the logistics of undertaking these experiments. One of the main practical considerations is how the biofilter media will be mounted on the pond surface. The biofilter cover design we tested in both the laboratory and field experiments described here will need to be modified, as supporting the biofilter on steel mesh is not practical at full-scale. Instead we envisage the biofilter soil being supported on a lightweight porous fabric that will float on top of the effluent pond. Floating wetland systems using such materials have been developed and deployed at several sites globally (Fig. 5). Such systems involve incorporation of plants into the plastic floating fabric to sequester nutrients from the effluent beneath. These structures could be modified to include a layer of methanotroph-rich soil either dispersed into the floating fabric or sitting on top of it.

The lab experiments in this study showed that for a typical New Zealand dairy effluent pond, a floating biofilter could offset about 145 tonnes of CO_2-e per year (based on emission rates from Craggs et al. 2008). In terms of CO_2-equivalent offsets, this equates to a value of about US $2.8K (NZ $3.5K) per year for a single farm, based on a CO_2-e price of $25/tonne (oxidation rates from the field filter were not quite as efficient, corresponding to an offset of

about NZ $2K per year per farm, but we have discussed how these field rates could be boosted to approximate those achieved in the lab). The key to developing biofilters as an effective CH_4 mitigation technology for dairy effluent ponds is to minimise their construction and operational costs. The results of this work, and previous research by the authors (Pratt et al. 2012a and b), have shown that soil biofilters are self-maintaining systems and that on-going maintenance should be minimal. If the floating biofilter installation cost can be limited to about US $15K (NZ $19K), then the payback period of the filter would be about 5 years. When scaled-up to New Zealand's estimated 8500 dairy farms that have anaerobic ponds, then a saving in carbon credits of about US $24 million (NZ $30 million) annually could be expected.

Figure 5: Example of a floating wetland designed for nutrient removal from a municipal/industrial wastewater treatment pond (with permission from Waterclean Technologies, NZ).

In addition to the economic benefits of carbon credits, further value from floating biofilters could come from odour mitigation, nutrient attenuation, hydrogen sulphide/ammonia removal (which was observed in the field biofilter study by Pratt et al. 2012a), as well as from the potential of harvesting biomass growing on top of the filters. Moreover, there is the potential for value-adding to floating biofilters through more advanced technologies, such as harvesting methanotroph-fixed carbon for bioplastic production, and using the vegetation on the floating filter for electricity generation via electron transfer through biomass (Helder et al. 2010). These additional dimensions to biofilters highlight their potential as an emerging green technology with potential benefits additional to GHG mitigation.

5 Conclusions

- Compost and volcanic soils demonstrated very high CH_4 oxidation rates (up to 27 g CH_4 m^3 h^{-1}) in biofilter covers used to offset CH_4 emissions from laboratory simulation anaerobic dairy effluent ponds.
- The measured CH_4 oxidation rates corresponded to a 99% removal of the CH_4 influx, which were similar to CH_4 emission rate from a typical dairy effluent pond.
- Methane oxidation rates by a field biofilter comprising compost field reached 18 g CH_4 m^3 h^{-1}.
- Nitrous oxide emissions from both the laboratory and field filters were negligible.
- The results clearly show that a biofilter cover design is very effective at offsetting CH_4 emissions from dairy effluent ponds.

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