



Discovery of a new method to reduce methane emissions from farm dairy effluent

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Abstract

Purpose The New Zealand Government requires gross emissions of biogenic methane (CH₄) to be reduced to 10% below 2017 levels by 2030. However, the amount of CH₄ emissions reported in the ‘Manure Management’ category of New Zealand’s Greenhouse Gas Inventory has increased by 123% since 1990. The purpose of this research was to determine the effect of treating farm dairy effluent (FDE) with polyferric sulphate (PFS) on CH₄ emissions.

Methods The effect of treating FDE with PFS on CH₄ emissions was measured at four scales: (i) 1-L gas jars in the laboratory, (ii) 1.1-m-deep × 150-mm-diameter pipe microcosms in the laboratory, (iii) large 3.4-m-deep × 0.47-m-diameter pipes on-farm, and (iv) 2-m-deep × 8.4-m-diameter (100,000 L) commercial effluent storage tanks on a farm. Gas emissions were captured by repeated discrete sampling and CH₄ concentrations were determined by gas chromatography.

Results We discovered that treating FDE with PFS at an average rate of 220 mg Fe L⁻¹ of FDE reduced CH₄ emissions by up to 99% and that this effect continued for an extended period of time (up to 2 months) after treatment. The PFS treatment also reduced CO₂ emissions by approximately 50% and reduced hydrogen sulphide emissions. PFS treatment resulted in a small increase in nitrous oxide (N₂O) emissions, but these emissions were very low and only represented < 3% of the total CO₂-e greenhouse gas emissions from the treated FDE.

Conclusions A new method to reduce CH₄ emissions from farm dairy effluent by up to 99% has been discovered.

Keywords Greenhouse gas · Methane · Effluent · Ponds · Polyferric sulphate · Carbon dioxide · Nitrous oxide · Hydrogen sulphide · Redox potential

1 Introduction

The New Zealand (NZ) Government’s Climate Change Response (Zero Carbon) Amendment Act 2019 set new greenhouse gas (GHG) reduction targets that will require gross emissions of biogenic methane (CH₄) to be reduced to 10% below 2017 levels by 2030 (New Zealand Government 2019). GHG emissions from the ‘Manure Management’ category in NZ’s Greenhouse Gas Inventory (NZ

GHG Inventory) represent the third largest contributor to NZ Agricultural GHG emissions after ‘Enteric Fermentation’ and ‘Agricultural Soils’ categories, accounting for 4.4% of the total agricultural sector GHGs in 2019 (MFE 2021a).

In 2019, CH₄ emissions from the ‘Manure Management’ category were equivalent to 1739 kt CO₂-e, which is an increase of 123% from the 1990 level of 779 kt CO₂-e (MFE 2021a). The majority of effluent storage ponds in NZ are on dairy farms and the amount of CH₄ emitted from those ponds has been estimated to represent approximately 10% of the total CH₄ emissions from NZ dairy farms (Pratt et al. 2012; Laubach et al. 2015).

Regional Councils in NZ require dairy farmers to construct large effluent ponds to provide sufficient storage capacity (in some cases up to 3 months) in order to reduce the risk of water pollution caused by effluent runoff or leaching during land application. This has led

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to an increase in the proportion of NZ dairy farms using effluent storage ponds for manure management from approximately 5% in 1990 to approximately 81% in 2017 (MPI 2017). Over 9700 NZ dairy farms now have effluent ponds, and the average pond volume is 1745 m³ and average storage capacity is approximately 86 days (MPI 2014). The NZ GHG Inventory calculations now assume that 8.5% of manure from lactating cows is deposited in the yard and stored in effluent ponds, which is an increase from 6% prior to 2015 (MPI 2019). Storage of dairy effluent in large ponds is not unique to NZ, but is widespread around the globe wherever dairy farming is a major farming activity (Owen and Silver 2015).

Methane is produced during effluent storage because of the anaerobic conditions that are present in effluent ponds. Under these anaerobic conditions a diverse population of microorganisms break down the complex organic matter in effluent through the sequential processes of (i) hydrolysis—conversion of proteins and carbohydrates into amino acids, fatty acids, and sugars; (ii) acidogenesis—conversion of amino acids and fatty acids into volatile fatty acids; (iii) acetogenesis—conversion of fatty acids into acetic acid, hydrogen (H₂), and carbon dioxide (CO₂); and finally, (iv) methanogenesis—conversion of acetic acid, H₂, and CO₂ into CH₄ (Paulo et al. 2015).

The daily capture and storage of farm dairy effluent (FDE) in effluent ponds creates an opportunity to treat the FDE to reduce the amount of CH₄ emitted into the atmosphere.

A new system for treating FDE (ClearTech®) has recently been developed using polyferric sulphate (PFS) to flocculate fine colloidal material in the effluent (e.g. soil, dung, organic matter) producing clarified water (CW) for recycling as yard wash water and treated effluent (TE) for irrigation onto farm land (Cameron and Di 2019). Polyferric sulphate is a polymerised form of ferric sulphate (FS) and is used to treat drinking water in many countries (Hendrich et al. 2001). Ferric sulphate is approved by the US Food and Drug Administration (FDA) as a ‘food additive’ and is affirmed as ‘generally recognised as safe’ (GRAS) for human consumption (FDA 2017). Iron is an essential dietary element and iron sulphate is used to increase the iron content of, and add flavour to, food (FDA 2017). A detailed description of the ClearTech® technology has been given by Cameron and Di (2019), and the environmental benefits of applying the treated effluent and clarified water onto farm land have been reported by Chen et al. (2019), Wang et al. (2019), and Chisholm et al. (2020).

The objective of the research reported in this paper was to determine the effect of treating FDE with PFS on CH₄ emissions, through a series of experiments of increasing scale.

2 Methods

2.1 Gas jar experiment—rates of PFS and methane emissions

The objective of the gas jar experiment was to (i) measure the effect of PFS treatment on CH₄ emissions from FDE and (ii) determine the relationship between rate of PFS treatment and CH₄ emissions.

The PFS was purchased from New China Chemicals Ltd. (Tianjin, China) and contained 20.1 ± 0.2% iron and 17.9 ± 0.1% sulphur (full details of the chemical composition are given in Cameron and Di (2019)). The FDE used in the experiments typically contained dung, urine, milk, soil, partially digested plant material, water, and cleaning chemicals (sodium hydroxide and sulphuric acid). The amount of PFS required to treat the FDE largely depended on the amount of solids contained in the FDE, as described by Cameron and Di (2019).

The experiment was conducted using 1.5 L glass jars which were filled with 1 L of FDE collected from the Lincoln University Dairy Farm, about 20 km south of Christchurch in Canterbury, NZ (43°38′S, 172°26′E). Lincoln University Dairy Farm comprises 160 ha of irrigated pasture with a seasonal supply milking herd of 555 Kiwi-cross cows (3.5 cows ha⁻¹) which are fed on grass/clover pasture only. There were 11 rates of PFS treatment, applied in 25-mg Fe L⁻¹ increments, ranging from 0 up to 250 mg Fe L⁻¹. There were four replicates of each treatment set out in a randomised block design in the laboratory and the experiment was conducted at 20 °C.

Each glass jar had a detachable screw cap with a rubber septum that allowed gas samples to be collected from the headspace above the effluent using a standard procedure for gas sampling (Di et al. 2007). The procedure involved attaching the screw cap to each jar and using a syringe to collect three gas samples through the septum at 30 min intervals between each sampling (i.e. at time = 0 min, time = 30 min, and time = 60 min). The screw caps were then removed until the next gas sampling. Measurements were conducted over an 8-day period following a single treatment.

The concentration of CH₄ gas in each sample was determined using a gas chromatograph (GC) (Model 8610C, SRI Instruments, CA, USA) with an automated Gilson GX-271 auto sampler (Gilson Inc., MI, USA) coupled to a flame ionised detector (FID). The GC used three HayeSep D packed pre-columns and two HayeSep D analytical columns. The carrier gases were H₂ and air, and the detector temperature setting was 370 °C.

Hourly GHG emissions were calculated based on the rate of increase in GHG concentration in the chamber

(from 0 to 60 min) corrected for temperature and the ratio of surface area to chamber volume (Selbie et al. 2014). Gas fluxes were calculated using the slope of headspace gas concentration change from the three samples collected on each sampling occasion (Hutchinson and Mosier 1981). Daily emissions were calculated using those hourly fluxes, assuming that the fluxes measured represented the average hourly flux of that day. Cumulative emissions were calculated by integrating the measured daily fluxes for the whole experimental measurement period. Methane emission data are expressed in CO₂ equivalents (CO₂-e) which were calculated using the standard global warming potential (GWP) factor of 25 to convert the amount of CH₄ emitted into CO₂ equivalents (MPI 2019).

2.2 Microcosm experiment #1—simulated effluent pond conditions

The objective of the first effluent pond microcosm experiment was to determine the effect of adding PFS on CH₄ emissions from FDE under simulated effluent pond conditions. The microcosm study used PVC pipes (1100 mm high × 150 mm diameter; 19.4 L volume) with end caps at the base and detachable gas collection caps at the top of each column. Each microcosm represented the physical dimensions of a 1-m vertical column of effluent in a shallow FDE pond. There were two treatments: (i) untreated FDE and (ii) treated effluent (TE). Seven replicate microcosms for each treatment were set out in a randomised block design in the laboratory and the experiment was conducted at 20 °C. Farm dairy effluent was collected from the Lincoln University Dairy Farm each day (excluding weekends) and the optimum rate of PFS required to achieve flocculation and clarification was determined daily using a standard laboratory ‘jar test’ method (ASTM D2035–13 2013; Cameron and Di 2019). The average amount of PFS added to each batch of effluent was 210 ± 14 mg Fe L⁻¹ of FDE. Five-hundred millilitres of FDE and TE was added to the replicate microcosms every workday for 4 weeks (i.e. excluding weekends) with the cumulative FDE volume equal to 10 L. The addition of each batch of effluent caused mixing within each microcosm and no mechanical mixing was employed. After 30 days, no more additions were made to the effluent columns; however, gas measurements continued for another 28 days.

Gas sampling was conducted once a day (during the working week) using a standard procedure for gas sampling (Di et al. 2007). The gas caps were attached to each column and three gas samples were taken with 30 min intervals between each sampling (i.e. at time = 0 min, time = 30 min, and time = 60 min). The gas caps were then removed until the next gas sampling occasion. The concentration of CH₄ gas was analysed using gas chromatography (as described above).

Additional gas samples were collected after 1 h of cover and the concentration of hydrogen sulphide (H₂S) was determined using an automated GC–MS (gas chromatograph mass spectrometry) (Wardencki 1998, 2000) using a Shimadzu GC–MS–QP2010 equipped with a CTC Analytics Combi-Pal auto-sampler (AOC-5000) for automated gas injection (Shimadzu Scientific Instruments (Oceania) Pty Ltd., NZ). The chromatography was performed using an Rtx-1 ms 30.0 m × 0.32 mm ID × 4 μm film thickness capillary column (Restek, USA). Helium was used as the carrier gas with the GC–MS set to a constant linear velocity of 48.0 cm s⁻¹. The column oven was initially held at 35 °C for 5.5 min, rapidly heated to 200 °C at 80 °C min⁻¹, and held for 2.44 min. Hydrogen sulphide was eluted at 1.32 min.

2.3 Microcosm experiment #2—rates of PFS and methane emissions

The objective of the second microcosm study was to determine the effect of a range of rates of PFS treatment on CH₄ emissions from FDE in a simulated 1-m depth of pond effluent. The experiment was conducted using the same microcosm equipment and gas sampling procedures described above. Farm dairy effluent was collected from the Lincoln University Dairy Farm each day (excluding weekends) and the optimum rate of PFS required to achieve flocculation and clarification was determined daily using a standard laboratory jar test method (ASTM D2035–13 2013; Cameron and Di 2019). The average amount of PFS added to each batch of effluent was 286 ± 24 mg Fe L⁻¹ of FDE. There were four treatments: (i) untreated FDE, (ii) effluent treated with PFS at the optimum rate to flocculate and clarify the effluent (286 mg Fe L⁻¹), (iii) effluent treated at half the optimum clarification rate (143 mg Fe L⁻¹), and (iv) effluent treated at one quarter the optimum clarification rate (72 mg Fe L⁻¹). There were three replicate columns per treatment set out in a randomised block design in the laboratory and the experiment was conducted at 20 °C. Two litres of each effluent treatment was added to the columns twice per week for 1 month. Gas samples were collected twice per week for 28 days and the concentration of CH₄ gas was determined using gas chromatography (as described above).

2.4 Macrocosm experiment #1—single treatment

A macrocosm evaluation of the laboratory derived experimental results was conducted using large PVC pipes (3.4 m deep × 0.47 m diameter; 590 L volume) installed in an in-ground concrete tank adjacent to the milking parlour on the Lincoln University Dairy Farm. These large columns represented vertical macrocosms of effluent that would be present in a typical farm dairy effluent pond, with the advantage that replicated treatments could be compared. Each column had

an end cap glued onto the bottom and a water trough collar attached to the top. The gas capture equipment was identical to that used for gas capture in nitrous oxide measurement research (Di et al. 2007) and involved placing an insulated gas capture chamber over the column with the edge of the chamber inserted into the water trough (thus giving an airtight gas seal). Each gas collection chamber had a small fan (120 mm diameter, 12 V, 1000 rpm; Jaycar Ltd.) which circulated the gas within the sealed head space of the column during gas sampling. The gas sampling and analysis procedures were the same as described above.

The objective of the experiment was to measure the effect of a single PFS treatment on CH₄ emissions from FDE. There were two treatments: (i) untreated FDE and (ii) FDE treated with PFS (TE). There were four replicates of each treatment set out in a randomised block design and the experiment was conducted at an average temperature of 19.2 ± 0.7 °C. Five-hundred and sixty litres of farm dairy effluent was pumped from the FDE storage pond on Lincoln University Dairy Farm into each macrocosm column leaving a head space height of 10 cm. A sub-sample of the effluent was taken to determine the optimum rate of PFS required to achieve flocculation and clarification using a standard laboratory jar test method (ASTM D2035–13 2013; Cameron and Di 2019). The amount of PFS added to the TE treatment was 200 mg Fe L⁻¹ of FDE. The PFS treatment was mixed into the effluent for 2 min using a hand held electric drill fitted with a paddle stirrer.

2.5 Macrocosm experiment #2—multiple inputs

The objective of the second field macrocosm experiment was to determine the effect of adding PFS using the on-farm ClearTech® effluent treatment system (Cameron and Di 2019) on CH₄ emissions during, and after, sequential additions of effluent into the macrocosm columns (i.e. simulating standard practice on a farm where effluent is treated each day and pumped into the effluent storage pond). There were three treatments: (i) untreated FDE, (ii) TE, and (iii) a mixture of treated effluent and clarified water (Mix) that was collected immediately after the PFS was mixed into the effluent but before settling of the TE had occurred (as described below). There were four replicates of each treatment set out in a randomised block design and the experiment was conducted at an average temperature of 17.3 ± 3.7 °C.

Using the same macrocosms as described above, 56 L of each effluent treatment was added to each replicated treatment column twice per week for 5 weeks until the columns were nearly full (560 L). Untreated FDE was pumped into the macrocosm columns at the same time that it was being pumped into the ClearTech® clarification tank (Cameron and Di 2019). Once the ClearTech® clarification tank was full the PFS solution was added automatically by the

ClearTech® computer-controlled pump at the optimal rate to achieve clarification of each batch of effluent (average rate used for the ten batches was 300 ± 14 mg Fe L⁻¹). After mixing for 15 min, 56 L of the mixture of treated effluent and clarified water (Mix) was then pumped into each treatment replicate column. Once complete, the ClearTech® mixing tank was allowed to settle for 3 h to enable the flocculated particles in the treated effluent to settle to the bottom of the tank (as described by Cameron and Di 2019); 56 L of TE was then pumped from the bottom of the tank into each replicated treatment column.

Gas sampling was conducted twice per week using the standard procedure for gas sampling and analysis as described earlier (Di et al. 2007). The gas sampling caps were then removed until the next gas sampling occasion and the concentration of CH₄ gas was determined using gas chromatography (as described earlier). The concentration of nitrous oxide (N₂O) and CO₂ were determined using the same gas chromatograph (GC) fitted with an electron capture detector (ECD) as well as the flame ionised detector (FID). N₂O was measured by ECD, and CO₂ was measured by FID (CO₂ was converted into CH₄ by a methaniser and then measured). Oxygen-free nitrogen and 10% CH₄ in argon were used as the carrier gas and ECD make-up gas, respectively. H₂ and air were used for the FID flame. The detector temperature of the ECD was set at 310 °C and the FID set at 370 °C. Daily emissions were calculated using the hourly flux, assuming that it represented the average hourly flux of the day (Hutchinson and Mosier 1981; Rochette 2011).

Redox potential values were measured at 3-m depth in each column using a Thermo pH 6 + pH/ORP meter (EUT01X245026W) with a double-junction, gel-filled ORP electrode plastic body 12 × 90 mm with BNC connector 5-m cable (ECFC7960205B) supplied by Thermo Fisher Scientific NZ Limited.

2.6 Farm-scale experiments

The objective of the farm-scale experiments was to measure the effect of PFS treatment of FDE on CH₄ emissions from effluent stored in typical effluent storage tanks used on a dairy farm. Two commercially available 100,000 L effluent storage tanks (KlipTanks®) were constructed on the Lincoln University Research Dairy Farm. One tank was used to store untreated FDE and the other tank used to store treated effluent (TE). A gas-tight PVC roof was installed over the top of each tank. Vents on each tank allowed the gas emissions to be captured and sampled when the vents were closed. During the time period between sampling events, the vents were left open to ensure that typical effluent tank storage conditions occurred.

Two farm-scale experiments were conducted in which the 100,000L storage tanks were filled by transferring five

batches of approximately 20,000 L of untreated FDE directly from the existing farm effluent sump into the ‘untreated FDE tank’ and by transferring five batches of approximately 20,000 L of treated effluent into the TE tank (leaving an equivalent headspace height of 570 mm). The tanks were filled in sequential batches to ensure that, as far as possible, the effluent composition was similar between the untreated batch and the treated batch produced each day on the farm. The average PFS treatment rate used in the two farm-scale experiments was 150 mg Fe L⁻¹ of FDE and the experiments were conducted at an average temperature of 23.6 ± 0.9 °C.

Gas sampling was conducted twice per week by closing the vents on each tank allowing the gas emissions to be captured and sampled. Once the vents were closed, a fan driven air mixing system (200 mm diameter, 240 V, mixing rate of 410 m³ per hour; Alaskon Ltd.) was used to mix the air in the enclosed headspace before three gas samples were taken with 90-min intervals between each sampling (i.e. at time = 0 min, time = 90 min, and time = 180 min). The vents were then left open until the next gas sampling occasion. The concentration of CH₄ gas was determined using gas chromatography (as described earlier).

2.7 Statistical analysis

Mean values and standard errors of the means (SEM) for each measured parameter were calculated for each experiment using Microsoft Excel (Microsoft Corporation USA). Regression analysis was also conducted using Microsoft Excel. The statistical analysis to test for significant differences between parameter values was conducted using two-tailed Student’s ‘*t*-tests’ using Microsoft Excel and analysis of variance (ANOVA) using Genstat Version 12.2 (VSN

International Limited). Where necessary, the data were log transformed to ensure homogeneity of residual errors.

3 Results

3.1 Lab gas jar experiment—rates of PFS and methane emissions

The amount of CH₄ emitted over the 8-day period was inversely related to the rate of PFS addition ($R^2=0.973^{***}$) (Fig. 1). There was a 98% reduction in the amount of CH₄ emitted at the highest rate of PFS treatment (250 mg Fe L⁻¹) and a 30% reduction at the lowest rate of treatment (25 mg Fe L⁻¹). The relationship between PFS rate and CH₄ emission shows that a large reduction was achieved at relatively low rates of PFS treatment; for example there was an 85% reduction when only half the optimum rate for coagulation and clarification was added (125 mg Fe L⁻¹).

3.2 Microcosm experiment #1

Treating FDE with a PFS solution (i) significantly ($P < 0.001$) reduced the average rate of CH₄ emission from treated effluent (TE) compared to untreated FDE (Fig. 2) and (ii) significantly ($P < 0.001$) reduced the total amount of CH₄ emitted over a 58-day period by 90%, compared to untreated farm dairy effluent (Table 1).

The reduction in CH₄ emission rate continued for 28 days after the last input of PFS (day 30).

Treatment of FDE with PFS also significantly ($P < 0.001$) reduced the concentration of hydrogen sulphide emitted from TE, compared to untreated FDE (Fig. 3).

Fig. 1 Relationship between total amount of methane (CH₄) emitted (g CO₂-e m⁻²) and PFS treatment rate (mg Fe L⁻¹)

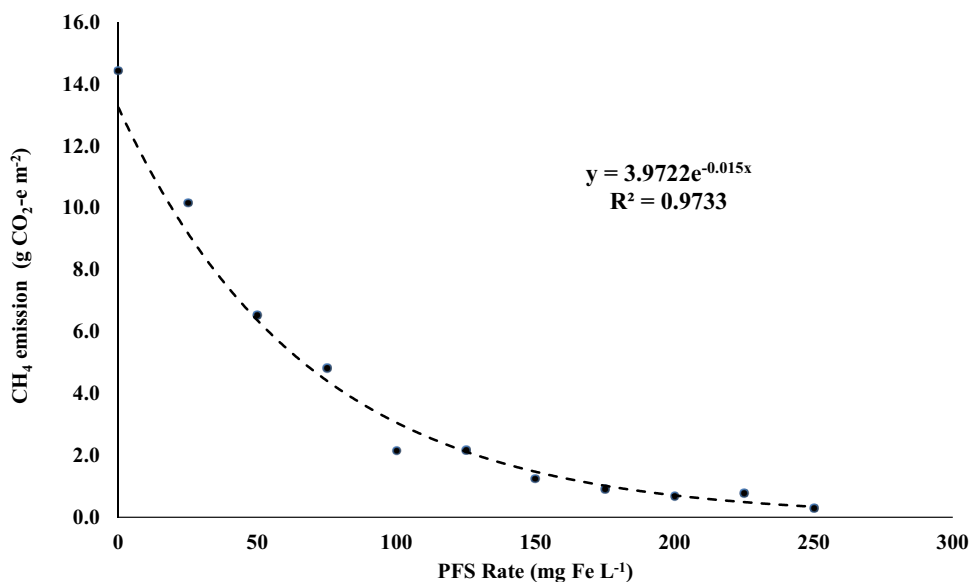
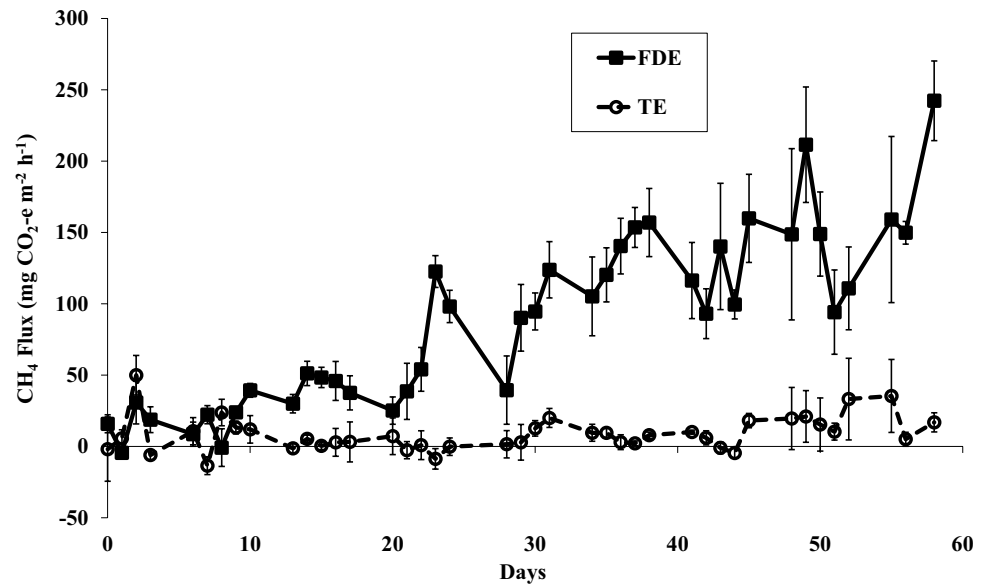


Fig. 2 Methane (CH_4) emission flux ($\text{mg CO}_2\text{-e m}^{-2} \text{h}^{-1}$) from untreated farm dairy effluent (FDE) and PFS-treated effluent (TE). Fresh FDE and TE were added to the columns daily for 30 days and measurements continued for a further 28 days after inputs stopped. Error bars are \pm SEM



3.3 Microcosm experiment #2—rates of PFS and methane emissions

Treating FDE with a PFS solution significantly ($P < 0.001$) reduced the average rate of CH_4 emission from all the TE treatments compared to the untreated FDE (Fig. 4).

Treating FDE with a PFS solution significantly ($P < 0.001$) reduced the total amount of CH_4 emitted over the 28-day period by 95% at the optimal clarification rate (286 mg Fe L^{-1}), by 96% at half the clarification rate (143 mg Fe L^{-1}), and by 72% at quarter the clarification rate (72 mg Fe L^{-1}), compared to untreated FDE (Table 1).

3.4 Macrocosm experiment #1—single input

The first field macrocosm experiment confirmed that a single PFS treatment of FDE (collected from an effluent storage pond) significantly ($P < 0.01$) reduced the average rate of CH_4 emission from the TE (Fig. 5).

Treating farm dairy effluent with a single input of PFS significantly ($P < 0.01$) reduced the total amount of CH_4 emitted over the 62-day period by approximately 92%, compared to untreated FDE (Table 1).

3.5 Macrocosm experiment #2—multiple inputs

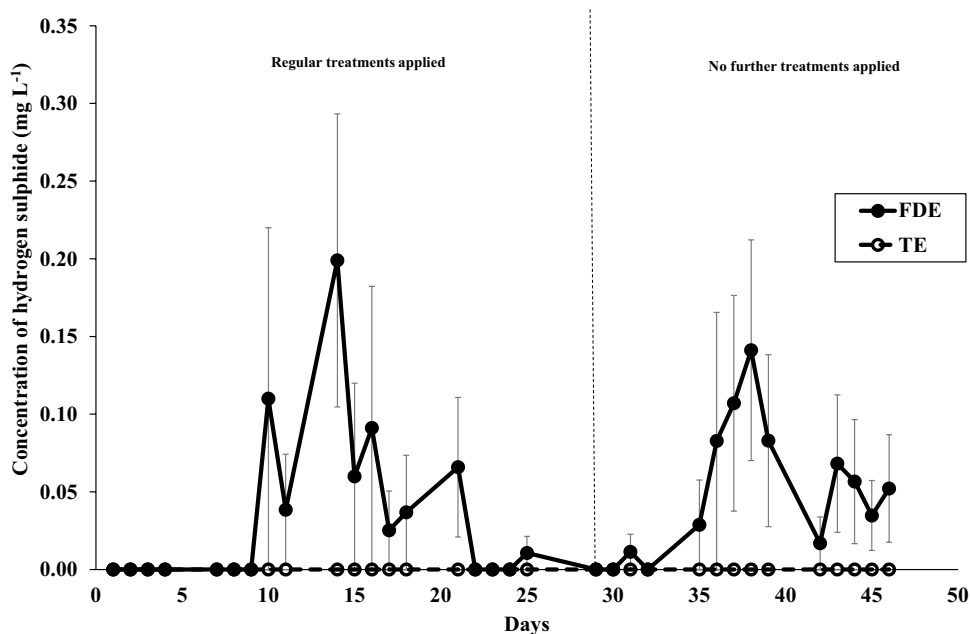
The second field macrocosm experiment confirmed that treating farm dairy effluent with PFS solution using

Table 1 Summary of experimental results and statistical analyses

Experiment name	Treatment details	Rate of PFS (mg Fe L^{-1})	Length of experiment (day)	Total amount of methane emitted over experimental period ($\text{g CO}_2\text{-e m}^{-2}$)			Reduction in amount of methane emitted (%)		<i>P</i> level
				FDE	TE	Mix	TE	Mix	
Microcosm #1	Multiple inputs	210	58	123.2 a	12.9 b	na	90	na	$P < 0.001$
Microcosm #2	- Rate 1	286	28	20.3 a	1.1 b	na	95	na	$P < 0.001$
	- Rate 2	143	28	20.3 a	0.8 b	na	96	na	$P < 0.001$
	- Rate 3	72	28	20.3 a	5.6 b	na	72	na	$P < 0.001$
Macrocosm #1	Single input	200	62	101.5 a	8.1 b	na	92	na	$P < 0.01$
Macrocosm #2	Multiple inputs	300	56	336.9 a	7.8 b	10.3 b	98	97	$P < 0.001$
Farm tanks	Multiple inputs	150	42	1051.4 a	na	2.4 b	na	99	$P < 0.01$

FDE farm dairy effluent, TE treated effluent, Mix mix of treated effluent and clarified water produced by the ClearTech system, na data not available. Numbers followed by different letters in each row indicate a statistically significant difference at the *P* level shown

Fig. 3 Concentration of hydrogen sulphide emissions (mg L^{-1}) from untreated farm dairy effluent (FDE) and PFS-treated effluent (TE). Error bars are \pm SEM



a sequence batch reactor (ClearTech®) significantly ($P < 0.001$) reduced the average rate of CH_4 emission from TE and a mix of treated effluent and clarified water (Mix), compared with untreated FDE (Fig. 6). In this experiment the PFS was mixed into freshly collected FDE using the ClearTech® treatment plant. Treatment occurred over the first 28 days only and the measurements showed that CH_4 emission mitigation continued for a further 28 days after ceasing PFS treatment (Fig. 6).

Treating farm dairy effluent with PFS (TE and Mix) significantly ($P < 0.001$) reduced the total amount of CH_4 emitted over a 56-day period by approximately 98% for the TE

treatment and by 97% for the Mix treatment, compared to untreated FDE (Table 1).

Treating FDE with PFS significantly ($P < 0.001$) reduced the total amount of carbon dioxide emitted over the 56-day period from both the TE (329 g m^{-2}) and Mix (402 g m^{-2}), compared to untreated FDE (681 g m^{-2}). The PFS treatment reduced the CO_2 emissions by 52% from the TE and by 41% from the Mix.

Although the amounts of N_2O emitted from the TE ($15.7 \text{ g CO}_2\text{-e m}^{-2}$) and Mix ($9.5 \text{ g CO}_2\text{-e m}^{-2}$) treatments were greater ($P < 0.001$) than that from the FDE ($2.8 \text{ g CO}_2\text{-e m}^{-2}$), the amounts emitted were very low and represented

Fig. 4 Methane (CH_4) emissions flux ($\text{mg CO}_2\text{-e m}^{-2} \text{ h}^{-1}$) from untreated FDE and PFS-treated effluent (TE) at three rates: (i) clarification rate (286 mg Fe L^{-1}), (ii) half the clarification rate (143 mg Fe L^{-1}), and (iii) quarter the clarification rate (72 mg Fe L^{-1}). Error bars are \pm SEM

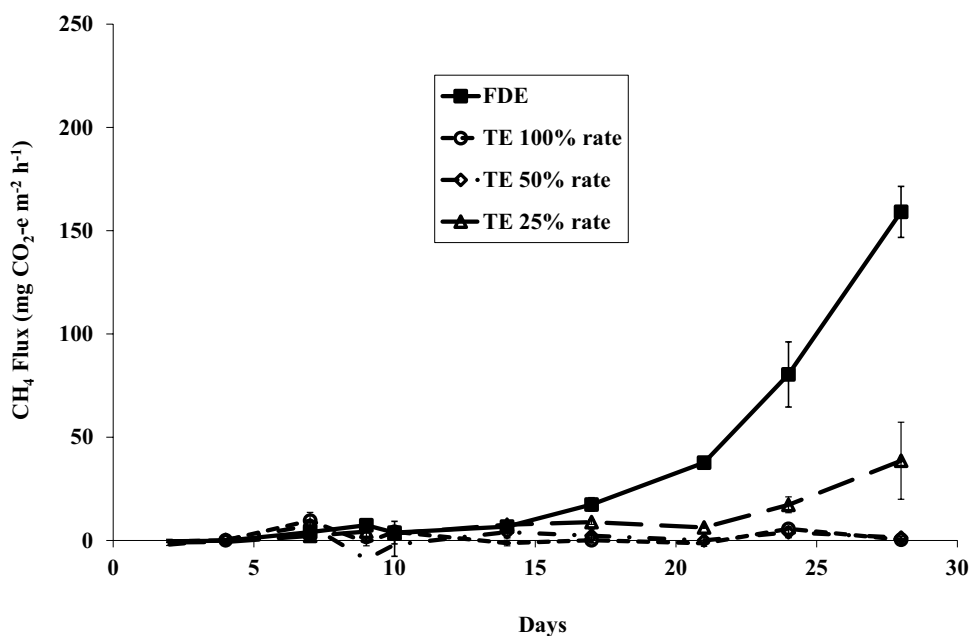
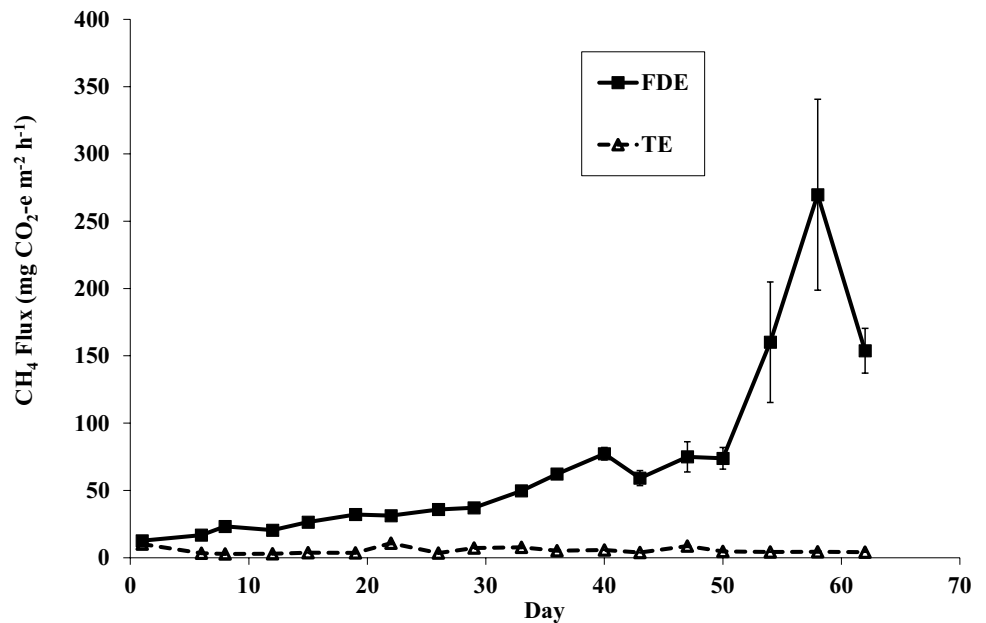


Fig. 5 Methane (CH_4) emissions flux ($\text{mg CO}_2\text{-e m}^{-2} \text{h}^{-1}$) from untreated farm dairy effluent (FDE) and PFS-treated effluent (TE) following a single input and mixing of PFS on day 0. Error bars are \pm SEM



less than 3% of the amount of CH_4 and CO_2 emitted from the treated FDE over the same period.

Redox potential (E_h) values in the untreated FDE macrocosms were significantly ($P < 0.001$) below those in the TE and Mix macrocosms for the majority of the trial period (up to day 35) (Fig. 7). The initial E_h value of the FDE was below -220 mV, whilst the initial redox values in the TE and Mix macrocosms were above zero. The redox values in the Mix remained above -150 mV for the full period of the experiment, whilst the values in the FDE dropped below -244 mV from day 25 onwards. The redox potential in the TE macrocosms dropped to

below -244 mV after day 36 and remained below this value for the remainder of the experiment.

3.6 Farm-scale experiments

The results of farm-scale measurements show that PFS was highly effective in reducing the CH_4 emission flux from TE throughout the full measurement period of 42 days compared to untreated FDE transferred to, and stored in, the large 100,000 L effluent tanks on a dairy farm (Fig. 8).

The results of the farm-scale experiments also show that PFS significantly ($P < 0.01$) reduced the total amount of CH_4

Fig. 6 Methane (CH_4) emission flux ($\text{mg CO}_2\text{-e m}^{-2} \text{h}^{-1}$) from untreated farm dairy effluent (FDE), PFS-treated effluent (TE), and a mix of treated effluent and clarified water (Mix). Fresh FDE, TE, and Mix were added to the columns until day 28 and measurements continued for a further 28 days after inputs stopped. Error bars are \pm SEM

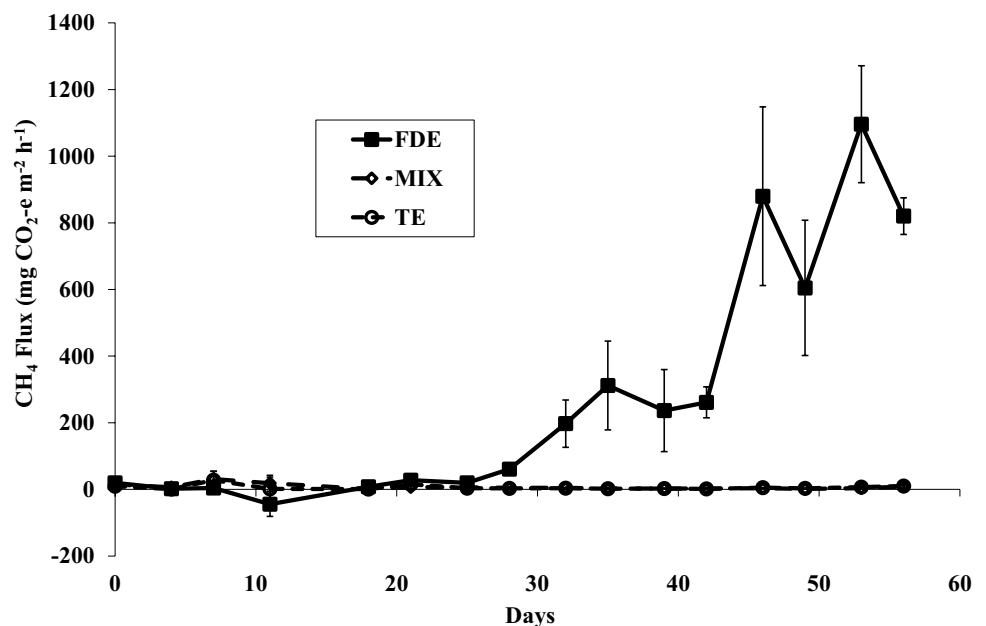
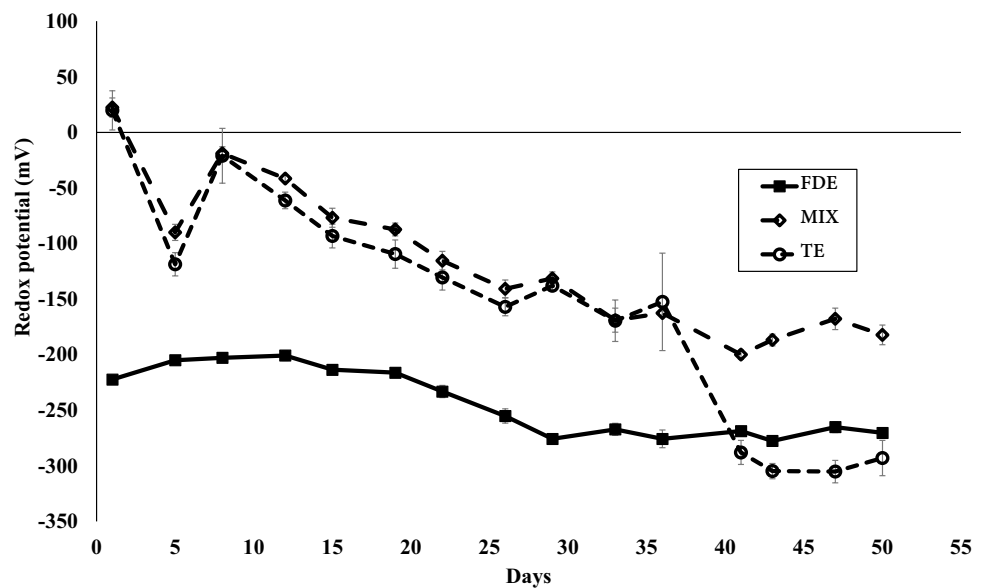


Fig. 7 Redox potential (E_h) values measured in the untreated farm dairy effluent (FDE) and PFS-treated effluent (TE) and a mix of treated effluent and clarified water (Mix) over a 50-day period. Error bars are \pm SEM



emitted from TE compared to untreated FDE transferred to, and stored in, the large 100,000-L effluent storage tanks on a dairy farm (Table 1). The PFS treatment reduced the total amount of CH_4 emitted from the effluent by an average of 99% (Table 1).

4 Discussion

4.1 Methane emission mitigation—amounts

The results show that treating FDE with PFS solution can significantly reduce CH_4 emissions by a substantial amount (up to 99%).

Laboratory data showed that the amount of CH_4 emitted was strongly related to the rate of PFS used to treat the FDE ($R^2 = 0.973^{***}$). There was an inverse curvilinear relationship ($y = 3.9722e^{-0.015x}$) between the amount of CH_4 emitted (y) and the rate of PFS added (x) showing that significant mitigation (e.g. > 85%) can be achieved at PFS rates 50% below the optimum rate required to achieve coagulation/clarification of FDE (Fig. 1). This relationship was confirmed in the microcosm experiment where there was a 96% reduction in CH_4 emissions at a PFS rate 50% below the optimum rate required for clarification. The microcosm and macrocosm data also showed that the CH_4 mitigation effect of PFS was consistent and that it continued for a considerable period of time (up to 2 months) after the PFS treatment had ceased.

The results of the farm-scale measurements, using large 100,000-L effluent storage tanks on a dairy farm, show that treating FDE with PFS significantly ($P < 0.01$) reduced the total amount of CH_4 emitted by an average of 99% and that

this reduction occurred over the full measurement period of 42 days. This demonstrates that the mitigation process is highly effective at farm-scale and that CH_4 emissions do not simply start immediately after treatment has ceased. This treatment longevity is of considerable practical importance because it means that the PFS can be used reliably on farms, with minimal risk of CH_4 emissions occurring during adverse events (e.g. equipment breakdowns), or when TE is stored in a pond without treatment for up to 42 days (or possibly longer, further research is underway to determine this).

Treating FDE with PFS also reduced the total amount of CO_2 emitted by 52% from the treated effluent compared to untreated FDE. The amount of N_2O emitted in the experiments represented less than 3% of the amount of CH_4 plus CO_2 emitted, which is in agreement with a review by Laubach et al. (2015) who concluded that direct N_2O emissions from FDE ponds are negligible.

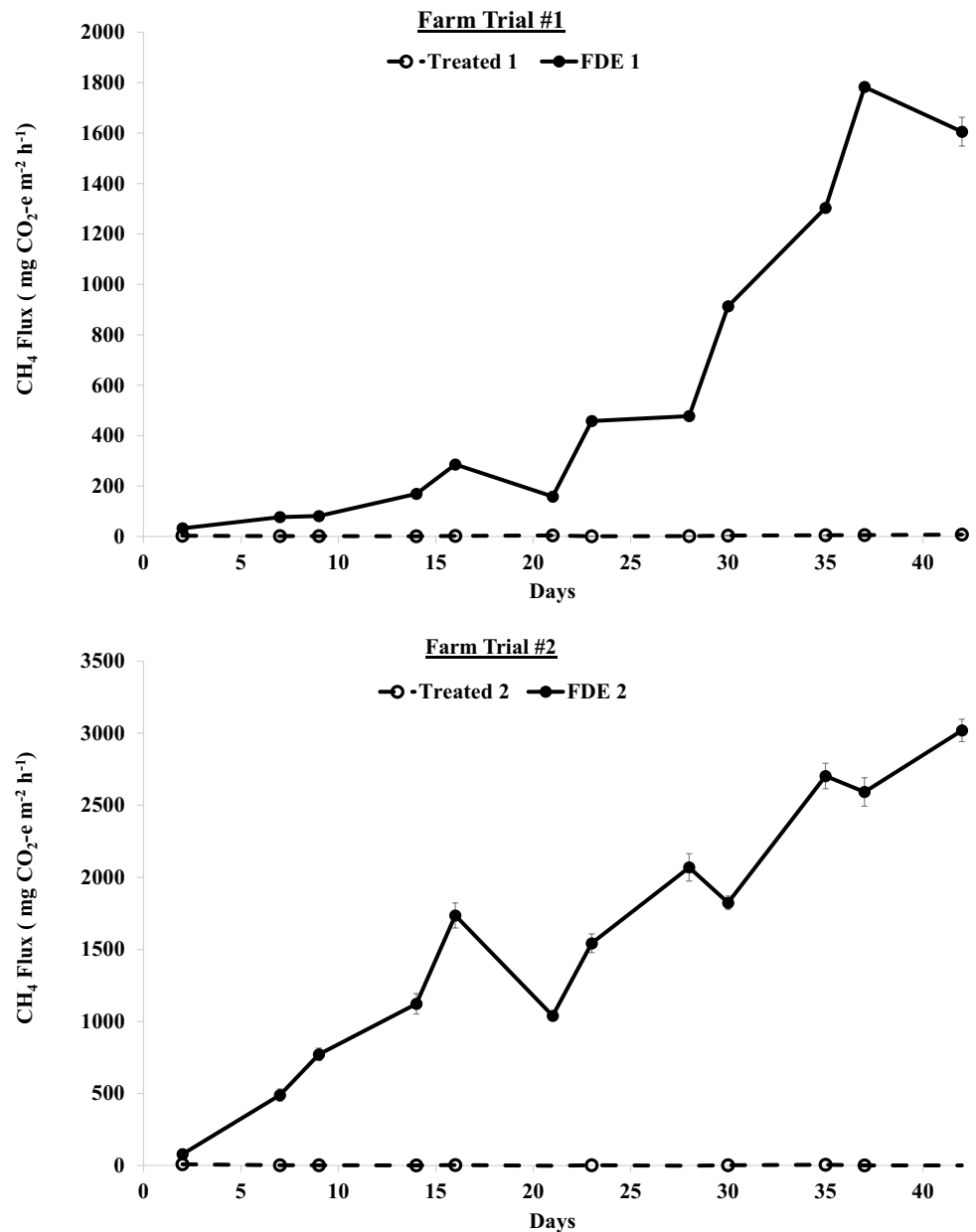
The results also show that CH_4 emissions from FDE can be reduced without increasing H_2S emissions. In fact, the experimental data show that the H_2S emissions are significantly reduced when FDE is treated with PFS. The reason for this reduction is that the ferrous iron (Fe^{2+}) and the sulphide (S^{2-}) produced in the treated effluent precipitate out as insoluble ferrous sulphide (FeS) (Firer et al. 2008):



4.2 Methane emission mitigation—mechanisms

We hypothesise that the reduction in CH_4 emissions following treatment of FDE with PFS can be attributed to three main mechanisms: (i) increased microbial

Fig. 8 Methane (CH₄) emission flux (mg CO₂-e m⁻² h⁻¹) from untreated farm dairy effluent (FDE) and PFS-treated effluent (TE) stored in large 100,000-L farm tanks in Farm Trial #1 and #2



competition for organic matter substrate due to the addition of sulphate and ferric ions, (ii) direct inhibition of methanogens due to sulphide and ferric ions, and (iii) anaerobic oxidation of CH₄.

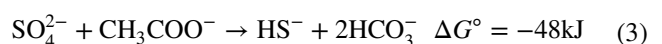
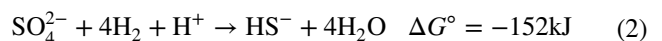
4.2.1 Increased competition for substrate

Addition of PFS to the FDE increased the concentration of sulphate (SO₄²⁻) and ferric (Fe³⁺) ions in the TE (e.g. in microcosm experiment #1 the SO₄²⁻ concentration increased from 4.5 ± 1.5 mg SO₄ L⁻¹ in the FDE to 600 ± 4 mg SO₄ L⁻¹ in the TE). Under anaerobic conditions in wetlands, high concentrations of SO₄²⁻ and Fe³⁺ ions have been reported

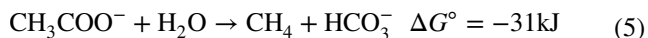
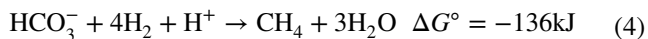
to inhibit methanogenesis due to sulphate-reducing bacteria (SRB) and ferric-reducing bacteria (FRB) out-competing the methanogens for substrate (e.g. acetate, CO₂) (Castro et al. 2000; Plugge et al. 2011; Paulo et al. 2015).

This competition occurs because the reduction of SO₄²⁻ to sulphide yields more Gibbs free energy (ΔG° = -152 kJ at 25 °C) than the process of methanogenesis (ΔG° = -136 kJ) (Eqs. 2–5) (Paulo et al. 2015).

Sulphate reduction:



Methanogenesis:



The effect of this increased competition for substrate by SRB and FRB is reflected in the redox data from macrocosm experiment #2, where the E_h values in the mixture of treated effluent and clarified water (Mix) remained above -150 mV. This is above the E_h value that normally occurs during CH_4 generation (approximately -244 mV at pH 7) (Table 2).

Under anaerobic conditions, SO_4^{2-} and Fe^{3+} species act as terminal electron (e^-) acceptors during anaerobic respiration coupled to the degradation of organic matter (Hulshoff Pol et al. 1998; Wild 1988). Therefore, CH_4 emissions remained consistently low from the Mix treatment throughout macrocosm experiment #2. In contrast, CH_4^+ emissions started to occur from the untreated FDE macrocosms once the redox potential value dropped below approximately -244 mV. The drop in redox potential to below -244 mV in the TE macrocosms, but not in the Mix macrocosms, may be attributed to the greater amount of volatile solids in the more concentrated TE ($6373 \pm 1060 \text{ g m}^{-3}$) compared to the Mix ($4022 \pm 568 \text{ g m}^{-3}$).

Although each redox reaction in Table 2 would have been 'poised' at the highest E_h value before moving to reactions lower on the redox cascade, these reactions are likely to occur concurrently at the boundaries between the redox potential of each reaction.

4.2.2 Direct inhibition

Although SO_4^{2-} is considered to be non-toxic towards anaerobic microorganisms, the product of its reduction, sulphide (Eqs. 2 and 3), is toxic to methanogens and has been reported to directly inhibit methanogenesis (Parkin et al. 1983; Karhadkar et al. 1987).

Similarly, the formation of ferric hydroxide, $\text{Fe}(\text{OH})_3$, and polynuclear ferric compounds during PFS treatment of the effluent may have reduced the CH_4 emissions because

Table 2 Typical oxidation reduction potentials (E_h) under anaerobic conditions (Stumm and Morgan 1996; Wild 1988)

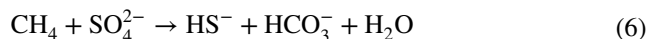
Reaction	E_h (mV at pH 5 and 25 °C)	E_h (mV at pH 7 and 25 °C)
$\text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}$	934	816
$\text{NO}_3^- + 2\text{H}^+ + 2e^- = \text{NO}_2^- + \text{H}_2\text{O}$	539	421
$\text{MnO}_2 + 4\text{H}^+ + 2e^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	634	396
$\text{Fe}(\text{OH})_3 + 3\text{H}^+ + e^- = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	172	-182
$\text{SO}_4^{2-} + 10\text{H}^+ + 8e^- = \text{H}_2\text{S} + 4\text{H}_2\text{O}$	-67	-215
$\text{CO}_2 + 8\text{H}^+ = \text{CH}_4 + 2\text{H}_2\text{O}$	-126	-244

of the activity of dissimilatory iron reducing bacteria (DIRB) (Van Bodegom et al. 2004; Zhou et al. 2014). DIRB can derive energy for growth by coupling the oxidation of organic matter with the reduction of Fe^{3+} , resulting in direct inhibition of methanogenesis (Van Bodegom et al. 2004). For example, ferric oxide-hydroxide compounds have been reported to suppress methanogenesis in flooded rice paddy soils (Van Bodegom and Stams 1999; Zhou et al. 2014).

4.2.3 Anaerobic oxidation of methane

Anaerobic oxidation of CH_4 (AOM) coupled to SO_4^{2-} reduction is reported to occur in wetlands (Segarra et al. 2015) and seawater (Suess 2014; Sivan et al. 2014; Shen et al. 2019):

Methane oxidation



Anaerobic oxidation of CH_4^+ is the main process that prevents the emission of CH_4 from marine and freshwater sediments into the atmosphere (Suess 2014; Sivan et al. 2014). AOM is reported to consume approximately 90% of the CH_4 produced in CH_4 seeps in the ocean floor (Sivan et al. 2014), and to consume over 50% of the CH_4 in freshwater wetlands (Segarra et al. 2015). The process is catalysed by communities of anaerobic methano-trophic archaea (ANME) and sulphate-reducing bacteria (SRB) (Segarra et al. 2015; Timmers et al. 2016). The presence of iron has also been shown to increase the rate of anaerobic oxidation of CH_4 in marine sediments (Sivan et al. 2014; Suess 2014) and in freshwater environments (Segarra et al. 2015; Timmers et al. 2016):

It therefore seems likely that the addition of SO_4^{2-} and Fe^{3+} ions into the FDE would have created similar AOM reactions to those described above, and that AOM would have reduced the amount of CH_4 emitted into the atmosphere from the TE and Mix microcosms compared to the FDE macrocosms. The occurrence of AOM may also help to explain why there was no increase in CH_4 emissions from the TE treatment in macrocosm experiment #2, despite the E_h values in the TE liquid dropping below -244 mV from day 30 onwards (Figs. 6 and 7).

4.3 Methane emission mitigation—an opportunity

We have discovered that treating FDE with a PFS solution can reduce CH_4 emissions by up to 99%. This is an important discovery because there is a need to decrease CH_4 emissions from agriculture as the NZ GHG Inventory shows that GHG emissions from the 'Manure Management' category increased by 123% from 779 kt $\text{CO}_2\text{-e}$ in 1990 to 1739 kt $\text{CO}_2\text{-e}$ in 2019 (MFE 2021a, b).

In 2019, GHG emissions in the NZ GHG Inventory Manure Management category represented 4.4% of GHG emissions from the total NZ agricultural sector, making it the third largest agricultural GHG category after ‘Enteric Fermentation’ and ‘Agricultural Soils’ categories, as defined in the NZ GHG Inventory (MFE 2021a). It has been estimated that manure management may represent about 10% of all the CH₄ emissions from a NZ dairy farm (Pratt et al. 2012; Laubach et al. 2015).

When considered in terms of global warming potential, the average reduction of 99% in CH₄ emissions measured in the farm effluent storage tank trials represent a considerable opportunity to reduce GHG emissions from individual NZ dairy farms (especially since more than 81% of them have large effluent storage ponds/tanks; MPI 2017). This reduction could help the NZ dairy industry to meet the NZ Government target of reducing CH₄ emissions on dairy farms to 10% below 2017 levels by 2030 (New Zealand Government 2019).

The discovery that treating FDE with PFS reduces CH₄ emissions by such a substantial amount creates a new opportunity for dairy farmers worldwide to reduce GHG emissions from FDE stored in effluent ponds or tanks.

5 Conclusions

This research discovered that treating FDE with PFS produced substantial reductions in CH₄ emissions (up to 99%) compared to untreated FDE.

Treating FDE with PFS also reduced the total amount of CO₂ emitted by approximately 50% compared to untreated FDE. The amount of N₂O emitted from all treatments represented less than 3% of the total amount of CH₄ and CO₂ emitted from treated FDE.

We hypothesise that the reductions in CH₄ emissions following treatment of FDE with PFS can be attributed to three mechanisms: (i) increased microbial competition for organic matter substrate, (ii) direct inhibition of methanogens, and (iii) anaerobic oxidation of CH₄.

A reduction of 99% in CH₄ emissions from farm dairy effluent ponds could help the NZ dairy industry to meet the NZ Government 2030 target of reducing CH₄ emissions on dairy farms to 10% below 2017 levels (New Zealand Government 2019). The technology has potential to be applied in a number of other countries where storage of animal effluents is common.

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