Biofiltration of methane from cow barns: effects of climatic conditions and packing bed media acclimatization

Franciele Fedrizzi\textsuperscript{a}, Hubert Cabana\textsuperscript{b}, Éliane M. Ndanga\textsuperscript{c} and Alexandre R. Cabral\textsuperscript{d,*}

\textsuperscript{a}Groupe Alphard, 5570 rue Casgrain, Montréal (Québec) H2T 1X9, Canada (formerly with Department of Civil Engineering, University of Sherbrooke)

\textsuperscript{b}Environmental Engineering Laboratory, Department of Civil Engineering, Université de Sherbrooke, Sherbrooke, Sherbrooke J1K 2R1, Canada.

\textsuperscript{c}Akvo, 6440, 13e Avenue, Montréal (Québec) H1X 2Y7, Canada (formerly with Department of Civil Engineering, University of Sherbrooke)

\textsuperscript{d}Geoenvironmental Group, Department of Civil Engineering, University of Sherbrooke, Sherbrooke, Quebec J1K 2R1, Canada.

*Corresponding author. Address: 2500, boul. de l’Université, Sherbrooke, Quebec J1K 2R1, Canada. Tel.: +1 819 821 7906; fax: +1 819 821 7974. alexandre.cabral@usherbrooke.ca

E-mail addresses: franciele.fedrizzi@usherbrooke.ca (F. Fedrizzi), hubert.cabana@usherbrooke.ca (H. Cabana), e.ndanga@usherbrooke.ca (E. M. Ndanga).

Abstract
The performance of biofiltration to mitigate CH4 emissions from cow barns was investigated in the laboratory using two flow-through columns constructed with an acclimatized packed bed media composed of inexpensive materials and readily available in an agricultural context. The biofilters were fed with artificial exhaust gas at a constant rate of 0.036 m3 h⁻¹ and low inlet CH4 concentration (0.22 g m⁻³ = 300 ppm). The empty-bed residence time (EBRT) was equal to 0.21 h. Additionally, in order to simulate temperature changes under natural conditions and determine the influence of such cycles on CH4 removal efficiency, the upper part of the biofilters were submitted to temperature oscillations over time. The maximum oxidation rate (1.68 μg CH4 gdw⁻¹ h⁻¹) was obtained with the commercial compost mixed with straw. Accordingly, it was considered as packing bed media for the biofilters. The CH4 removal efficiency was affected by the temperature prevailing within the biofilters, by the way in which the cooling-warming cycles were applied and by the acclimatization process. The shorter the cooling-warming cycles, the more oxidation rates varied. With longer cycles, CH4 removal rates stabilized and CH4 removal efficiencies attained nearly 100% in both biofilters, and remained at this level for more than 100 days, irrespective of the temperature at the top of the biofilter, which was – at times - adverse for microbiological activity. The first order rate constant for CH4 oxidation kinetics of the entire system was estimated at 15 h⁻¹. If such rate could be transposed to real field conditions in Canada, home to nearly 945,000 dairy cows, biofiltration may be applied to efficiently abate between 2 x 10⁶ and 3 x 10⁶ t yr⁻¹ of CO₂ equivalent (depending on how estimates are performed) from bovine enteric fermentation alone.

Keywords: Biofiltration; packing bed media; acclimatization; cooling-warming cycles; animal houses
1. Introduction

Global livestock agriculture was responsible for 12 to 18% (5.2 to 7.9 Pg CO₂ eq year⁻¹) of the anthropogenic greenhouse gas (GHG) emissions annually (Ecofys, 2016; IPCC, 2014; Shafer et al., 2011) and agricultural emissions of GHGs could increase to 7.9 – 8.5 Pg CO₂ eq year⁻¹ by 2050 (Shafer et al., 2011). According to USEPA (2012), approximately 37% of global agricultural methane (CH₄) and nitrous oxide (N₂O) arise from direct animal and manure emissions. Enteric CH₄ comprises 17 and 3.3% of global CH₄ and GHG emissions, respectively, and is largely derived from ruminant livestock (Ecofys, 2016; USEPA, 2012, 2010). CH₄ is a powerful GHG, with an estimated global warming potential of 28 to 36 times higher than that of carbon dioxide (CO₂), over 100 years (Myhre et al., 2013; USEPA, 2017).

In Canada, emissions associated with the agriculture sector accounted for 8% of the country’s total GHG emissions in 2015 (0.06 Pg CO₂ eq year⁻¹), 28% of which were CH₄ emissions. Emissions from enteric fermentation accounted for 42% (0.025 Pg CO₂ eq year⁻¹) of total GHG emissions associated with the agriculture sector in the country (Government of Canada, 2015). The dairy sector is the third most important farming sector in Canada (Government of Canada, 2017a). The dairy industry is concentrated in the central region of Canada, namely Quebec and Ontario, with 82% of Canada’s dairy farms (Government of Canada, 2017a). Of the total GHG emissions of the Province of Quebec, 40.8% are attributed to bovine enteric fermentation (MDDEP, 2014).

On Quebec’s dairy farms, cows remain confined to barns during the winter. Inside a typical barn, the air exchange occurs at a rate of 6 to 7 times every hour to maintain a high-quality environment for the animals. This leads to high air exchange rates, with exhaust gas containing
very low CH$_4$ concentrations. Canada wants to reduce footprint emissions and is therefore looking for viable alternatives (Government of Canada, 2015; MDDEP, 2014).

The main CH$_4$ emissions reduction strategies studied within the animal husbandry context are: 1) robust ecologically-based management practices and technologies; 2) best feeding management and nutrition; 3) use of rumen modifiers; and 4) increasing animal production through genetics and other management approaches (Knapp et al., 2014; Shafer et al., 2011). As far as mitigation of GHG emissions is concerned, biofiltration is a technique that has been commonly applied in agricultural and industrial sectors (Akdeniz et al., 2011), but has received relatively less attention when it comes to abatement of CH$_4$ emissions in animal houses. Typical CH$_4$ concentrations inside animal houses range between 5 and 100 mg m$^{-3}$ (milking cow). The average ventilation rate is 1000 m$^3$ h$^{-1}$ (Melse and Werf, 2005). One important difficulty in using biofilters for CH$_4$ biotic oxidation is related to such high air exhaust rates, because it requires long residence times and very large biofilters (Melse and Werf, 2005; Schmidt et al., 2004). Inside the biofilter, methanotrophs are able to oxidize the CH$_4$ under aerobic conditions, while generating oxidation by-products such as water (H$_2$O) and carbon dioxide (CO$_2$). Their activity depends on the presence of sufficient concentrations of both CH$_4$ and O$_2$, and is therefore limited in their distribution inside of the biofilter by diffusion of CH$_4$ and O$_2$ (De Visscher et al., 1999; Scheutz and Kjeldsen, 2004, 2003). The biofilter internal bed temperature has a profound influence on the methanotrophic activity in oxidizing CH$_4$. Most methanotrophs are mesophiles, whose optimum operating temperatures lie between 25 and 35 $^\circ$C (Boeckx and Cleemput, 1996; Scheutz et al., 2009; Scheutz and Kjeldsen, 2004), although methanotrophic communities have the capability of adapting to temperatures varying between 0 and 55 $^\circ$C (Einola et al., 2007; Humer and Lechner, 1999; Scheutz et al., 2009). Temperature influences not only biotic activity;
it also affects CH₄ and O₂ diffusion coefficients (Delhomènie and Heitz, 2005; Gómez-Borraz et al., 2017).

One may expect that under severe climatic conditions, such as observed in Canadian winters, CH₄ oxidation in biofilters constructed to treat cow barn exhaust gas, would come to a halt. Considering the conditions prevailing in dairy cow barns in Canada (high exhaust rates and low CH₄ concentrations), it is essential to assess the influence of temperature variation cycles in the efficiency of biofilters to mitigate CH₄ emissions. The purpose of this study was to verify the validity of the hypothesis that, given proper acclimatization of the packing bed media, large biofilters constructed with common farm materials can sustain biotic CH₄ oxidation under typical Canadian dairy farm conditions, even under adverse temperature conditions for biofiltration.

2. Materials and Methods

2.1. Selection of packing bed media

Commercial compost (comm-comp), sawdust (swd), straw (stw), manure compost (man-comp) and woodchips (wd-chp) were tested. Laboratory experiments were performed by mixing these materials at different ratios: (a) comm-comp/swd/stw (1:1:1 v/v); (b) comm-comp/stw (1:1 v/v); (c) comm-comp/swd (1:1 v/v); (d) comm-comp/swd (1:2 v/v); (e) comm-comp/swd (2:1 v/v), (f) man-comp/wd-chp (1:1 v/v); and (g) man-comp/wd-chp/stw (1:1:1 v/v).

The final selection of the packing bed media for the biofilter was based on CH₄ oxidation rates obtained during short-term activation tests. The latter were carried out over a period of 6 weeks, in 18.9-litre buckets filled with 5 L of the tested media. CH₄ loading (injection of 10 mL of pure CH₄) was performed twice a week. For the determination of oxidation rates, gas samples were taken immediately after loading and 3 hours later. The CH₄ concentrations were then obtained
using a 3000A gas chromatograph (Agilent Technologies). Both CH$_4$ loading and samples
collection were performed using syringes. The moisture content of the packing media tested
ranged from 43% to 64% and the density ranged from 0.3 g cm$^{-3}$ to 0.5 g cm$^{-3}$.

2.2. Acclimatization process

The same experimental set-up used for the packing bed media selection was adopted for the
acclimatization process. CH$_4$ was loaded periodically and the CH$_4$ concentrations within the
buckets were monitored over time to ensure that the samples were continually exposed to its
presence. Acclimatization was performed in duplicate prior to each of the three subsequent
biofilter tests (described below). The duo acclimatization biofilter test forms what is referred
herein as a biofilter set.

For Sets A and B, the CH$_4$ initial loading increased with time (from 200 mL to 3000 mL of pure
CH$_4$), while for Set C the CH$_4$ loading remained constant (1000 mL of pure CH$_4$). One important
aspect of the acclimatization process is that from Sets A to B and B to C, 50% of the packing bed
used in one set was reused to build the biofilters of the following set. In addition, the lids of the
buckets were opened periodically to allow proper aeration of the samples. The acclimatization
process lasted approximately one month for each set.

2.3. Biofiltration tests

Flow-through column experiments were performed in duplicates to reproduce biofilters operating
under the winter conditions of a typical cow barn containing 150 cows. As shown in Figure 1,
the 11.8-L Plexiglas® columns were filled with 7.6 L of the selected packing bed media. In the
reduced scale of the laboratory, the modelled biofilters were fed with a constant exhaust gas rate
equal to 0.036 m$^3$ h$^{-1}$ and the inlet CH$_4$ concentration equal to 0.22 g m$^{-3}$ (or 300 ppm; personal communication with Daniel Massé – Agriculture and Agri-Food Canada). This exhaust rate (0.036 m$^3$ h$^{-1}$) was calculated based on the following premises: a minimum ventilation rate equal to 1000 m$^3$ day$^{-1}$ per cow (Turnbull and Huffman (1988); Table 1) and a very large biofilter (1300 m$^3$, was our preliminary design value). The latter premise was based on Melse and Werf (2005), who concluded that very large biofilters are necessary to abate CH$_4$ emissions from animal houses. Adopting these values resulted in an empty-bed residence time (EBRT) equal to 0.21 h. The responses of the biofilters were monitored during three relatively long testing periods. Set A was carried out from May to December 2013, Set B from March to November 2014 and Set C from March to July 2015.

To determine the influence of temperature cycles on the efficiency of the biofilters to abate CH$_4$ emissions, we submitted the biofilters to temperature oscillations simulating natural cycles undergone by biofilters exposed to winter conditions. The cooling system consisted of copper tubing wrapped around the exterior of the Plexiglas® column and connected to a temperature-controlled bath (constant temperature circulator – Polystat®). Only the upper part of the biofilter was cooled to simulate a condition whereby frost penetrates to a certain depth. The temperature of the bath was controlled throughout the experimental period, leading to variable temperature gradients within the biofilters. Thermocouples allowed monitoring of the temperature of the packing bed media at three different heights, 5 cm, 20 cm and 40 cm from the base of the biofilter.

Figure 1. Biofiltration system used in the flow-through column experiments.
The CH₄ loading rate was controlled by a flow meter, whereas the inlet and outlet gas concentrations were monitored using an infrared gas chromatograph, GC 3000A (Agilent Technologies) and mass flowmeters (Omega FMA-2600A). Throughout the experiments, the concentrations of the incoming gas mixture were maintained as follows: CH₄ = 300 ppm, CO₂ = 500 ppm and O₂ = 400 ppm. The gas mixture was bubbled through water to avoid drying the packing bed media.

2.3.1. Calculations of CH₄ removal efficiencies during biofilter tests

Assuming the CH₄ oxidation in the biofilters occurs following first order kinetics (Girard et al., 2011; Melse and Werf, 2005) and plug-flow conditions, the first order rate constant for CH₄ oxidation (K) can be calculated using Equation:

\[
K = \frac{\ln(C_{in}) - \ln(C_{out})}{EBRT}
\]  
Equation 1

where \(C_{in}\) is the inlet CH₄ concentration (g m\(^{-3}\)), \(C_{out}\) is the outlet CH₄ concentration (g m\(^{-3}\)), K is the first order rate constant for CH₄ oxidation (h\(^{-1}\)) in the biofilter system, with removal (or CH₄ oxidation) removal efficiency (RE) calculated by mass balance, according to Equation, as follows:

\[
RE = \frac{(C_{in} - C_{out})}{C_{in}}
\]  
Equation 2
The temperatures associated with $C_{in}$ and $C_{out}$ were not the same. Consequently, the first order kinetic constant is expected to vary along the height of the biofilter. In this case, we propose to use an “apparent” $K$ – denoted herein as $K_{\text{apparent}}$ – which reflects the response of the entire biofilter.

By combining Equations 1 and 2, the biofilter volume can be estimated using Equation 3, as follows:

$$V = -\ln(1 - RE) \times \frac{Q}{K_{\text{apparent}}}$$  

Equation 3

3. **Results and discussion**

3.1. **Selection of packing bed media**

In the biofilter system, the filling material supports and sustains the development of the methanotrophic consortia. CH$_4$ oxidation can be achieved by using organic filter packing materials such as compost, sawdust, straw, wood chips, bark mulch, composted wastes and peat, as well as mixtures of these materials (Chang et al., 2016; Melse and Hol, 2017; Pawłowska et al., 2011; Wei et al., 2016). The tests to select the most adequate packing bed media were performed in an acclimatization bucket with 7 mixtures of different materials and the CH$_4$ oxidation rate results are presented in Table 1.

Table 1 - CH$_4$ oxidation rates from the tested packing bed media.
The maximum oxidation rate \((1.68 \, \mu g \, CH_4 \, g_{dw}^{-1} \, h^{-1})\) was obtained with the commercial compost mixed with straw. The results in Table 1 shows that other materials or combinations thereof could be used as packing bed media. In fact, given the high standard deviations obtained, combinations such as compost-sawdust (average rate = \(0.85 \, \mu g \, CH_4 \, g_{dw}^{-1} \, h^{-1}\)) might be also be employed. According to Pawłowska et al. (2011), the type of filter bed material was not an important factor in determining methanotrophic capacity, in cases where oxygen was supplied to the biofilter.

For comparative purposes, in landfill biofilters constructed with mixtures of organic materials, \(CH_4\) oxidation rates range from 5.3 to 10.7 \(\mu g \, CH_4 \, g_{dw}^{-1} \, h^{-1}\) at 22 °C (Gebert et al., 2003). Canadian farms produce large quantities of agricultural residues each year, in particular wheat straw (Li et al., 2012). Compost, in addition to being available in dairy farms, has a high \(CH_4\) oxidation capacity and has been commonly used for this purpose (Haubrichs and Widmann, 2006; Roncato and Cabral, 2012; Wei et al., 2016). Consequently, since one of the main purposes of this research was to apply biofiltration by the use of reusable and inexpensive materials, the compost-straw mixture seemed the most appropriate choice for the packing bed media.

### 3.2. Acclimatization process

Figure 2 shows the acclimatization process of Biofilter 1, which was quite similar to what was observed for Biofilter 2. Only one segment (out of several) is presented herein. It is representative of the overall behavior during acclimatization. In the first two experiments (Sets A and B), the \(CH_4\) loading was not maintained constant throughout the process, in fact it increased with time. For Set C, the \(CH_4\) loading was maintained constant. The intention with the first two
sequences was not only to adapt the system faster, but also to evaluate its capacity to oxidize ever increasing CH\textsubscript{4} loadings. This idea was eventually abandoned to focus on acclimatizing the materials to be used in the biofilter experiments.

Figure 2. Representative acclimatization segments for experimental Sets A, B and C. Temperatures were kept constant at 21 °C. Even though the beginning of each segment is shown to start at Day 0, segments A, B and C were obtained sequentially.

The CH\textsubscript{4} concentrations in the bucket were obtained as quickly as possible following injection of CH\textsubscript{4}. In some cases, the CH\textsubscript{4} concentration decreased quite quickly and the first measurements showed values already lower than the loading value, indicating that the system responded rapidly, as far as biotic oxidation of CH\textsubscript{4} is concerned. It is assumed herein that reductions in CH\textsubscript{4} concentrations are the result of biotic oxidation processes. We did not perform microbiological tests that would confirm the presence of – or an increase in – active methanotrophic consortia, such as documented by Gebert et al. (2003), Humer and Lechner (1999) and Karthikeyan et al. (2017, 2016).

As shown in Figure 2, the CH\textsubscript{4} concentrations steadily decreased to levels below detectable limits within a day or two following loading. Considering the acclimatization patterns shown in Figure 2, which became repetitive with time, it was concluded that the acclimatization process, for the materials selected, can be considered achieved within approximately 2 weeks. According to Melse and Werf (Melse and Werf, 2005), an adaptation period is fundamental for establishing the equilibrium between the availability of CH\textsubscript{4} and the amount of methanotrophs in the packing bed (start-up period). Therefore, the results in Figure 2 corroborate the start-up time-frame value
obtained by Melse and Werf (2005) for a biofilter filled with expanded perlite and garden compost (60:40 v/v). The acclimatization pattern is also quite similar to that found by Visscher et al. (2001), who observed steady state methanotrophic activity during soil incubation tests in 2-liter bottles. Furthermore, according to Brandt et al. (2016), the ideal start-up time-frame is 95 days for biofilters filled with mixtures of organic (composted leaves) and three non-organic materials (sponge-based material, blast furnace slag and expanded vermiculite) (60:40 v/v).

3.3. Biofiltration tests

Figure 3 shows the CH$_4$ removal efficiency as a function of temperature for Biofilters 1 and 2, during three monitoring sets (A, B and C). It can be observed that for Sets A1 (Biofilter 1) and A2 (Biofilter 2), fast cooling-warming cycles were applied for up to 80 days. For Set A1, the CH$_4$ removal efficiency (RE in Equation 2) oscillated in the very beginning but rapidly stabilized at approximately 60%. This stabilization seems to be supported by the packing bed media temperatures in the lower, non-cooled, part of the biofilters (5 to 20 cm from the base; Figure 1), where temperatures remained sufficiently high (between 15 and 18 $^\circ$C) to allow sustained CH$_4$ biotic oxidation. For Set A2 (Biofilter 2), the CH$_4$ removal efficiency oscillated for a longer period of time (Figure 3). Towards Day 80, it started to stabilize at approximately 50%, which is slightly lower than the value obtained with the other biofilter. This could be attributed to the much lower temperatures at the top of Biofilter 2, which reached -5 $^\circ$C (in Set A1 it reached ~0$^\circ$ C), while at the base it remained at ~18 $^\circ$C. In addition, the temperature at mid-height (20 cm) remained relatively stable at ~13 $^\circ$C. Despite the fact that most methanotrophs are mesophiles with optimum operating temperatures varying between 25 and 35 $^\circ$C (Boeckx and Cleemput, 1996; Scheutz et al., 2009), the temperatures observed at the base of the biofilters
were sufficiently high (average of 19 °C) throughout the testing period to sustain methanotrophic activity.

Figure 3. CH₄ removal efficiency as a function of temperature for three monitoring sets for both Biofilters, 1 and 2. (A) Set A, (B) Set B, and (C) Set C. The different sets are associated with different acclimatization processes. The thick line-and-arrows in Sets A and B indicate the end of short cooling-warming cycles and the beginning of longer cycles.

After 80 days (line-and-arrows in Figure 3; Sets A1 and A2), following a rapid increase in temperature, the system gradually cooled down. The intention was to allow for greater stabilization of CH₄ removal efficiencies. In Set A1, this resulted in stabilization of the CH₄ removal efficiency at nearly 100%, whereas in Set A2 it remained at the same level as before cooling, i.e. 50%. Towards the end of the last cooling cycle for Sets A1 and A2 (∼ Day 190), the lowest temperatures were recorded at the top of both biofilters (A1 = -3.9 °C and A2 = -4.2 °C). In the case of Biofilter 1, the temperature dropped at mid-height along the biofilter, which resulted in a sharp decrease in RE values, albeit still rather high (60%). In the case of Biofilter 2, RE values slowly decreased (with some spikes) reaching 30% by the end of the test.

Early in the experimental period (up to 80 days) of Sets B1 and B2 (Figure 3), the cooling-warming cycles were even faster than in Sets A1 and A2. This led to lower packing bed media temperatures at mid-height and at the base of the biofilters than for Sets A1 and A2. In this case, the CH₄ removal efficiency oscillations followed the same pattern as the temperature variations.
at the top of the biofilter (40 cm; Figure 1). Nearly one month after the beginning of Sets B1 and B2, RE values started to stabilize, averaging 16.3% (Biofilter B1), and 28.6% (Biofilter B2).

After 80 days (line-and-arrows in Figure 3), when the temperature of the system was high, a new cooling cycle was started for Sets B1 and B2. Sets A1 and A2 were not subjected to such a slow cycle. In Set B1, this resulted in a decrease in CH$_4$ removal efficiency that followed a pattern similar to that of the temperature at the top of the biofilter (40 cm). After RE attained its minimum value (26%) at Day 166, the CH$_4$ removal efficiency started to increase and the packing bed media temperature at the base and mid-height of the biofilters reached a constant value, whereas it continued to decrease at the top. At the end of the long cooling segment, the value RE in Set B1 oscillated around 50%. As the system was warmed back again, efficiencies increased to nearly 100%. Set B2 responded in a somewhat different way to the slow cooling cycle. Indeed, the CH$_4$ removal efficiency oscillated rapidly between 50 and 100%, but ultimately showed a decreasing pattern over time, reaching a minimum in the vicinity of 30%, when the temperature at the top of the biofilter was below zero (~ -1.7 °C) and the temperature at mid-height was at its lowest point (~ 11 °C) during this cooling cycle. Following an abrupt warming of the system, efficiency values rapidly increased to almost 70%, where they remained relatively stable, albeit with some oscillation. In summary, as far as cooling cycles for Sets B1 and B2 are concerned, the faster they were, the lower the CH$_4$ removal efficiencies. More importantly, the results in Figure 3 showed that CH$_4$ removal efficiency is not only affected by temperature, but also by the way in which the cooling-warming cycles were applied.

In Sets C1 and C2 (Figure 3), it was decided to apply cooling-warming cycles following a much slower pace for both biofilters (Sets C1 and C2). Two complete cycles lasted 128 days. It can be observed that both biofilters behaved in a quite similar manner, with CH$_4$ removal efficiencies
remaining very high (~100%) throughout the duration of Sets C1 and C2, i.e. even during
cooling cycles.

Temperature plays an important role in CH₄ removal efficiency. The exothermic reaction of CH₄
removal was maintained even during cold spells, simulated here by lowering the temperature of
the temperature-controlled bath and cooling system (Figure 1). Temperatures from the middle to
the bottom of the biofilters remained sufficiently high (Figure 3), with temperatures near the
bottom remaining nearly unchanged throughout the cycles, and temperatures at mid-height
decreasing by only a few degrees.

Another important factor to consider when analyzing the responses of the duplicate biofilters is
that 50% of the packing bed used in one set was reused to build the biofilters of the following
set. This, combined with the relatively stable temperatures at 5 and 20 cm and with the prolonged
testing periods of Sets A and B (that served as acclimatization for Set C), led to the nearly
constant efficiency (~ 100%) observed during Set C. If this behavior can be transposed to real
field conditions in dairy farms, biofilter efficiency to mitigate CH₄ emissions would be expected
to improve with time.

Table 2 summarizes several cases of application of the biofiltration technique to reduction of
CH₄ emissions. As far as biofiltration of exhaust air from animal houses is concerned, to our
knowledge, very few studies have been performed with inlet CH₄ concentrations as low as the
one considered herein (0.22 g m⁻³; or 300 ppm), which reproduces conditions found during
winter in dairy farm barns, in Canada. Girard et al. (2011) loaded their biofilters with CH₄
concentrations varying from 0.16 to 2.8 g m⁻³ and obtained CH₄ removal efficiencies between 36
– 51%. Melse and Hol (2017) tested three different biofilters with loadings ranging from 0.001 to
0.1 g m⁻³, with inlet gas temperatures ranging from 15 to 23 °C during the monitoring period,
and observed no significant difference between the inlet and outlet CH$_4$ concentrations during 12 months of monitoring.

Table 2 - Application of the biofiltration technique to reduction of CH$_4$ emissions.

3.4. **Biofilter design**

Typical CH$_4$ concentrations in cow barns are 5-100 mg m$^{-3}$ at an average ventilation rate of 1000 m$^3$ h$^{-1}$ milking cow$^{-1}$ (naturally ventilated) (Melse and Werf, 2005). For a regular-sized barn of 100 milking cows, the average exhaust gas rate is approximately 60,000 m$^3$ h$^{-1}$ (Melse and Werf, 2005). The latter is proportional to the typical range for a 150-cow dairy barn in Canada, i.e. 102,600 m$^3$ h$^{-1}$ (personal information from Daniel Massé, from Sherbrooke Research and Development Centre, Agriculture and Agri-Food Canada). For winter time, this rate falls to 6,480 m$^3$ h$^{-1}$, which is the value adopted herein.

In this section we designed a full scale biofilter based on the above-mentioned exhaust rate and on the results obtained under the conditions tested, i.e. constant exhaust gas rate (0.036 m$^3$), low inlet CH$_4$ concentration (0.22 g m$^{-3}$; or 300 ppm), and empty-bed residence time (EBRT) fixed at 0.21 h. In addition, we assumed CH$_4$ oxidation occurred following first order kinetics (Girard et al., 2011; Melse and Werf, 2005). The kinetics constant ($K_{\text{apparent}}$) values indicated in Table 3 were used to determine biofilter volumes for winter conditions ($V_{\text{winter}}$).

Table 3 - Biofilter volumes representative of a regular-sized farm of 100 dairy cows during winter, according to the experimental sets.
Winter operating conditions may severely limit the activity of some methanotroph groups (Gebert et al., 2003; Scheutz et al., 2009). Despite this fact, the $K_{\text{apparent}}$ values presented in Table 3 are somewhat closer to the $K$ value of 7.5 h$^{-1}$ found by Girard et al. (2011) for pig barn exhaust air, and much higher than $K$ values reported in the literature pertaining to biofiltration of CH$_4$ in animal houses, i.e. $K = 2$ to 2.5 h$^{-1}$ (Melse and Werf, 2005; Streese and Stegmann, 2003).

According to the literature related to biofiltration of exhaust air from animal houses, extremely large biofilter volumes would be required (Girard et al., 2011; Melse and Werf, 2005; Veillette et al., 2012). Melse and Werf (2005) state that this technology would not be a realistic option. However, we propose applying the approximate average value obtained from Sets C1 and C2, i.e. 1000 m$^3$. The latter would reflect conditions prevailing in a well-established biofilter after a proper acclimatization process. Considering a 1-m thick biofilter, the necessary footprint would be approximately 1000 m$^2$, or 100 m x 10 m. This is a fairly large biofilter that would be placed along the length of the barn. The volume obtained confirmed the initial premises made (see section 2.3), where a 7.6-liter biofilter simulated a 1300-m$^3$ biofilter in the laboratory.

4. Conclusions

This paper addresses the use of biofiltration to mitigate CH$_4$ emissions under operating conditions simulating those of dairy cow barns in Canada. The packing bed media used for the laboratory biofilter (a mixture of commercial compost and straw) was selected based on the highest oxidation rate. The CH$_4$ removal efficiency was affected by the temperature prevailing within the biofilters, by the way in which the cooling-warming cycles were applied and by the acclimatization process. As far as the latter, one important factor to consider was the fact that part of the packing bed media used in one set was reused in subsequent biofilter tests of the
following set. The shorter the cooling-warming cycles, the more the oxidation rates varied. With
the longer cycles of the last set, which better simulate nature, CH\textsubscript{4} removal rates stabilized and
CH\textsubscript{4} removal efficiencies greatly improved, attaining nearly 100%.

The number of cows in dairy farms is estimated at 945,000 in Canada (Government of Canada, 2017b). Therefore, if the efficiencies obtained in this research can be transposed to real field
conditions, biofiltration would be able to abate from $2 \times 10^6$ and $3 \times 10^6$ t yr\textsuperscript{-1} of CO\textsubscript{2} equivalent
(USEPA, 2017).

Acknowledgements

This study received financial support from the Dairy Farmers of Canada and Agriculture and Agri-
Food Canada (Dairy Cluster Project ED#1), and MITACS (Canada), with CNPq and Vale (Brazil)
(Fellowship # IT08498). The Authors would like to acknowledge the invaluable help of Jean-Guy
Lemelin, technician, and Carolina Lopera, graduate student.

References

https://doi.org/10.1016/j.biortech.2011.01.058

https://doi.org/10.4141/A03-109


IPCC, 2014. Climate change 2014 - mitigation of climate change. New York, NY, USA.


<table>
<thead>
<tr>
<th>Packing bed media</th>
<th>Mixing ratio</th>
<th>Number of samples</th>
<th>Average CH₄ oxidation rate (µg CH₄ g₉dₙ⁻¹ h⁻¹)</th>
<th>Min. – Max. (µg CH₄ g₉dₙ⁻¹ h⁻¹)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>comm-comp/swd/stw</td>
<td>1:1:1</td>
<td>11</td>
<td>0.74</td>
<td>0 – 1.15</td>
<td>0.36</td>
</tr>
<tr>
<td>comm-comp/stw</td>
<td>1:1</td>
<td>11</td>
<td>0.94</td>
<td>0.41 – 1.68</td>
<td>0.40</td>
</tr>
<tr>
<td>comm-comp/swd</td>
<td>1:1</td>
<td>11</td>
<td>0.75</td>
<td>0.32 – 1.00</td>
<td>0.23</td>
</tr>
<tr>
<td>comm-comp/swd</td>
<td>1:2</td>
<td>11</td>
<td>0.62</td>
<td>0.45 – 0.87</td>
<td>0.15</td>
</tr>
<tr>
<td>comm-comp/swd</td>
<td>2:1</td>
<td>11</td>
<td>0.85</td>
<td>0.38 – 1.41</td>
<td>0.29</td>
</tr>
<tr>
<td>man-comp/wd-chp</td>
<td>1:1</td>
<td>10</td>
<td>0.37</td>
<td>0 – 0.83</td>
<td>0.37</td>
</tr>
<tr>
<td>man-comp/wd-chp/stw</td>
<td>1:1:1</td>
<td>11</td>
<td>0.53</td>
<td>0 – 1.36</td>
<td>0.48</td>
</tr>
</tbody>
</table>

¹ comm-comp: commercial compost; swd: sawdust; stw: straw; man-comp: manure compost; wd-chp: wood chips.

dw = dry weight.
Table 2 - Application of the biofiltration technique to reduction of CH$_4$ emissions.

<table>
<thead>
<tr>
<th>Working bed volume (L)</th>
<th>Packing media</th>
<th>Inlet CH$_4$ concentration (%v/v)</th>
<th>Inlet load (g CH$_4$ m$^{-3}$ h$^{-1}$)</th>
<th>EBRT (h)</th>
<th>CH$_4$ oxidation efficiency (%)</th>
<th>Monitoring time (days)</th>
<th>Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.85</td>
<td>Wood pine bark chips, perlite and compost (50:35:15)</td>
<td>0.17 – 0.18</td>
<td>15.6 – 16.0</td>
<td>0.073</td>
<td>36 – 51</td>
<td>100 – 250</td>
<td>18 – 22$^1$</td>
<td>Gómez-Cuervo et al. (2016)</td>
</tr>
<tr>
<td>17.7</td>
<td>Stones</td>
<td>0.73</td>
<td>68.5</td>
<td>0.071</td>
<td>35</td>
<td>365</td>
<td>24$^1$</td>
<td>Ramirez et al. (2012a)</td>
</tr>
<tr>
<td>18</td>
<td>Inorganic gravel material</td>
<td>0.3</td>
<td>20</td>
<td>0.1</td>
<td>70</td>
<td>N. Av</td>
<td>N. Av.</td>
<td>Veillette et al. (2012)</td>
</tr>
<tr>
<td>17.7</td>
<td>Inorganic gravel material</td>
<td>0.025 – 0.420</td>
<td>2.4 – 38.0</td>
<td>0.07</td>
<td>36 – 51</td>
<td>N. Av</td>
<td>20 – 25$^1$</td>
<td>Girard et al. (2011)</td>
</tr>
<tr>
<td>2</td>
<td>Mature municipal solid waste compost</td>
<td>0.75 – 1.00</td>
<td>976 – 1,305</td>
<td>1.33</td>
<td>99 – 100</td>
<td>180</td>
<td>20 – 24$^2$</td>
<td>Pawłowska et al. (2011)</td>
</tr>
<tr>
<td>17.5</td>
<td>Cylindrical pieces of an inorganic gravel material</td>
<td>0.13 – 0.98</td>
<td>3.0 – 22.4</td>
<td>0.292</td>
<td>94 – 100</td>
<td>30</td>
<td>20 – 26$^1$</td>
<td>Nikiema and Heitz (2009)</td>
</tr>
<tr>
<td>18</td>
<td>Cylindrical pieces of an inorganic gravel material</td>
<td>0.13 – 1.00</td>
<td>12 – 95</td>
<td>0.072</td>
<td>50 – 37</td>
<td>19</td>
<td>N. Av</td>
<td>Nikiema et al. (2009)</td>
</tr>
<tr>
<td>160</td>
<td>Expanded perlite and garden compost (40:60)</td>
<td>0.075 – 0.850</td>
<td>0.1 – 25.0</td>
<td>0.12 – 1.33</td>
<td>85 – 18</td>
<td>60</td>
<td>4.7 – 21.12</td>
<td>Melse and Werf (2005)</td>
</tr>
<tr>
<td>17,000</td>
<td>Wood chip</td>
<td>0.0032</td>
<td>N. Av</td>
<td>0.0004</td>
<td>N. Av.</td>
<td>180 – 365</td>
<td>15 – 22$^2$</td>
<td>Melse and Hol (2017)</td>
</tr>
<tr>
<td>47,000</td>
<td></td>
<td>0.0031</td>
<td>N. Av</td>
<td>0.0007</td>
<td>N. D.</td>
<td>180 – 365</td>
<td>23 – 25$^2$</td>
<td></td>
</tr>
<tr>
<td>110,000</td>
<td></td>
<td>0.0117</td>
<td>N. Av</td>
<td>0.001</td>
<td>N. D.</td>
<td>180 – 365</td>
<td>22 – 23$^2$</td>
<td></td>
</tr>
<tr>
<td>7.85</td>
<td>Composted leaves and sponge-based material</td>
<td>4 – 56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composted leaves and blast furnace slag</td>
<td>0.17 – 3.6</td>
<td>3.0 – 148.8</td>
<td>0.12 – 0.71</td>
<td>4 – 54</td>
<td>188</td>
<td>19 – 36$^1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composted leaves and expanded vermiculite</td>
<td>13 – 95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$ Ambient temperature; $^2$ Inlet gas temperature;

N. Av. = Not available.

N. D. = No significant difference was found between inlet and outlet concentration.
Table 3 - Biofilter volumes representative of a regular-sized farm of 100 dairy cows during winter, according to the experimental sets.

<table>
<thead>
<tr>
<th></th>
<th>$K_{\text{apparent}}$ (h$^{-1}$)</th>
<th>$V_{\text{winter}}$ (m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A1</td>
<td>4.6</td>
<td>1168.7</td>
</tr>
<tr>
<td>Set A2</td>
<td>3.0</td>
<td>914.6</td>
</tr>
<tr>
<td>Set B1</td>
<td>1.9</td>
<td>1598.8</td>
</tr>
<tr>
<td>Set B2</td>
<td>3.2</td>
<td>1232.3</td>
</tr>
<tr>
<td>Set C1</td>
<td>17.5</td>
<td>837.1</td>
</tr>
<tr>
<td>Set C2</td>
<td>12.7</td>
<td>996.1</td>
</tr>
</tbody>
</table>
Figure 1
Figure 3

Substrate temperature (°C)

Set A1
Set B1
Set C1

Substrate temperature (°C)

Set A2
Set B2
Set C2

Time (days)

CH₄ oxidation efficiency, η (%)

Beginning of longer cooling-warming cycles

η

cooling system

40 cm
20 cm
5 cm