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

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Abstract

The performance of biofiltration to mitigate CH_4 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 m^3 h^{-1} and low inlet CH_4 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 CH_4 removal efficiency, the upper part of the biofilters were submitted to temperature oscillations over time. The maximum oxidation rate (1.68 μg $_{CH4}$ g_{dw}^{-1} h^{-1}) was obtained with the commercial compost mixed with straw. Accordingly, it was considered as packing bed media for the biofilters. 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. The shorter the cooling-warming cycles, the more oxidation rates varied. With longer cycles, CH_4 removal rates stabilized and CH_4 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 CH_4 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 10^6 and 3 x 10^6 t yr^{-1} of CO_2 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 CO_2 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 CO_2 eq $year^{-1}$ by 2050 (Shafer et al., 2011). According to USEPA (2012), approximately 37% of global agricultural methane (CH_4) and nitrous oxide (N_2O) arise from direct animal and manure emissions. Enteric CH_4 comprises 17 and 3.3% of global CH_4 and GHG emissions, respectively, and is largely derived from ruminant livestock (Ecofys, 2016; USEPA, 2012, 2010). CH_4 is a powerful GHG, with an estimated global warming potential of 28 to 36 times higher than that of carbon dioxide (CO_2), 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 CO_2 eq $year^{-1}$), 28% of which were CH_4 emissions. Emissions from enteric fermentation accounted for 42% (0.025 Pg CO_2 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_2O) 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 °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 °C (Einola et al., 2007; Humer and Lechner, 1999; Scheutz et al., 2009). Temperature influences not only biotic activity;

it also affects CH_4 and O_2 diffusion coefficients (Delhoménie and Heitz, 2005; Gómez-Borraz et al., 2017).

One may expect that under severe climatic conditions, such as observed in Canadian winters, CH_4 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 CH_4 concentrations), it is essential to assess the influence of temperature variation cycles in the efficiency of biofilters to mitigate CH_4 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 CH_4 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 CH_4 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. CH_4 loading (injection of 10 mL of pure CH_4) was performed twice a week. For the determination of oxidation rates, gas samples were taken immediately after loading and 3 hours later. The CH_4 concentrations were then obtained

111 using a 3000A gas chromatograph (Agilent Technologies). Both CH_4 loading and samples
112 collection were performed using syringes. The moisture content of the packing media tested
113 ranged from 43% to 64% and the density ranged from 0.3 g cm^{-3} to 0.5 g cm^{-3}.

114

115 **2.2. Acclimatization process**

116 The same experimental set-up used for the packing bed media selection was adopted for the
117 acclimatization process. CH_4 was loaded periodically and the CH_4 concentrations within the
118 buckets were monitored over time to ensure that the samples were continually exposed to its
119 presence. Acclimatization was performed in duplicate prior to each of the three subsequent
120 biofilter tests (described below). The duo acclimatization biofilter test forms what is referred
121 herein as a biofilter set.

122 For Sets A and B, the CH_4 initial loading increased with time (from 200 mL to 3000 mL of pure
123 CH_4), while for Set C the CH_4 loading remained constant (1000 mL of pure CH_4). One important
124 aspect of the acclimatization process is that from Sets A to B and B to C, 50% of the packing bed
125 used in one set was reused to build the biofilters of the following set. In addition, the lids of the
126 buckets were opened periodically to allow proper aeration of the samples. The acclimatization
127 process lasted approximately one month for each set.

128

129 **2.3. Biofiltration tests**

130 Flow-through column experiments were performed in duplicates to reproduce biofilters operating
131 under the winter conditions of a typical cow barn containing 150 cows. As shown in Figure 1,
132 the 11.8-L Plexiglas® columns were filled with 7.6 L of the selected packing bed media. In the
133 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.

157 The CH_4 loading rate was controlled by a flow meter, whereas the inlet and outlet gas
158 concentrations were monitored using an infrared gas chromatograph, GC 3000A (Agilent
159 Technologies) and mass flowmeters (Omega FMA-2600A). Throughout the experiments, the
160 concentrations of the incoming gas mixture were maintained as follows: CH_4 = 300 ppm, CO_2 =
161 500 ppm and O_2 = 400 ppm. The gas mixture was bubbled through water to avoid drying the
162 packing bed media.

163

164 **2.3.1. Calculations of CH_4 removal efficiencies during biofilter tests**

165 Assuming the CH_4 oxidation in the biofilters occurs following first order kinetics (Girard et al.,
166 2011; Melse and Werf, 2005) and plug-flow conditions, the first order rate constant for CH_4
167 oxidation (K) can be calculated using Equation :

168

169 $$K = \frac{ln(C_{in}) - \ln(C_{out})}{\text{EBRT}} \qquad \text{Equation 1}$$

170

171 where C_{in} is the inlet CH_4 concentration (g m^{-3}), C_{out} is the outlet CH_4 concentration (g m^{-3}), K is
172 the first order rate constant for CH_4 oxidation (h^{-1}) in the biofilter system, with removal (or CH_4
173 oxidation) removal efficiency (RE) calculated by mass balance, according to Equation , as
174 follows:

175

176 $$RE = \frac{(C_{in} - C_{out})}{C_{in}} \qquad \text{Equation 2}$$

177

178 The temperatures associated with C_{in} and C_{out} were not the same. Consequently, the first order
179 kinetic constant is expected to vary along the height of the biofilter. In this case, we propose to
180 use an "apparent" K – denoted herein as $K_{apparent}$ – which reflects the response of the entire
181 biofilter.

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

184

185 $$V = -\ln(1 - RE) \times \frac{Q}{K_{apparent}}$$ Equation 3

186

187 **3. Results and discussion**

188 **3.1. Selection of packing bed media**

189 In the biofilter system, the filling material supports and sustains the development of the
190 methanotrophic consortia. CH_4 oxidation can be achieved by using organic filter packing
191 materials such as compost, sawdust, straw, wood chips, bark mulch, composted wastes and peat,
192 as well as mixtures of these materials (Chang et al., 2016; Melse and Hol, 2017; Pawłowska et
193 al., 2011; Wei et al., 2016). The tests to select the most adequate packing bed media were
194 performed in an acclimatization bucket with 7 mixtures of different materials and the CH_4
195 oxidation rate results are presented in Table 1.

196

197 Table 1 - CH_4 oxidation rates from the tested packing bed media.

198

The maximum oxidation rate (1.68 μg $_{CH4}$ 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 μg $_{CH4}$ 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 μg $_{CH4}$ 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

222 sequences was not only to adapt the system faster, but also to evaluate its capacity to oxidize
223 ever increasing CH_4 loadings. This idea was eventually abandoned to focus on acclimatizing the
224 materials to be used in the biofilter experiments.

225

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

229

230 The CH_4 concentrations in the bucket were obtained as quickly as possible following injection of
231 CH_4. In some cases, the CH_4 concentration decreased quite quickly and the first measurements
232 showed values already lower than the loading value, indicating that the system responded
233 rapidly, as far as biotic oxidation of CH_4 is concerned. It is assumed herein that reductions in
234 CH_4 concentrations are the result of biotic oxidation processes. We did not perform
235 microbiological tests that would confirm the presence of – or an increase in – active
236 methanotrophic consortia, such as documented by Gebert et al. (2003), Humer and Lechner
237 (1999) and Karthikeyan et al. (2017, 2016).

238 As shown in Figure 2, the CH_4 concentrations steadily decreased to levels below detectable
239 limits within a day or two following loading. Considering the acclimatization patterns shown in
240 Figure 2, which became repetitive with time, it was concluded that the acclimatization process,
241 for the materials selected, can be considered achieved within approximately 2 weeks. According
242 to Melse and Werf (Melse and Werf, 2005), an adaptation period is fundamental for establishing
243 the equilibrium between the availability of CH_4 and the amount of methanotrophs in the packing
244 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 ^{o}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 °C (in Set A1 it reached ~0^{o} C), while at the base it remained at ~18 °C. In addition, the temperature at mid-height (20 cm) remained relatively stable at ~13 ^{o}C. Despite the fact that most methanotrophs are mesophiles with optimum operating temperatures varying between 25 and 35 °C (Boeckx and Cleemput, 1996; Scheutz et al., 2009), the temperatures observed at the base of the biofilters

268 were sufficiently high (average of 19 °C) throughout the testing period to sustain methanotrophic
269 activity.

270

271 Figure 3. CH_4 removal efficiency as a function of temperature for three monitoring sets for both
272 Biofilters, 1 and 2. (A) Set A, (B) Set B, and (C) Set C. The different sets are
273 associated with different acclimatization processes. The thick line-and-arrows in Sets
274 A and B indicate the end of short cooling-warming cycles and the beginning of longer
275 cycles.

276

277 After 80 days (line-and-arrows in Figure 3; Sets A1 and A2), following a rapid increase in
278 temperature, the system gradually cooled down. The intention was to allow for greater
279 stabilization of CH_4 removal efficiencies. In Set A1, this resulted in stabilization of the CH_4
280 removal efficiency at nearly 100%, whereas in Set A2 it remained at the same level as before
281 cooling, i.e. 50%. Towards the end of the last cooling cycle for Sets A1 and A2 (~ Day 190), the
282 lowest temperatures were recorded at the top of both biofilters (A1 = -3.9 °C and A2 = -4.2 °C).
283 In the case of Biofilter 1, the temperature dropped at mid-height along the biofilter, which
284 resulted in a sharp decrease in RE values, albeit still rather high (60%). In the case of Biofilter 2,
285 RE values slowly decreased (with some spikes) reaching 30% by the end of the test.

286 Early in the experimental period (up to 80 days) of Sets B1 and B2 (Figure 3), the cooling-
287 warming cycles were even faster than in Sets A1 and A2. This led to lower packing bed media
288 temperatures at mid-height and at the base of the biofilters than for Sets A1 and A2. In this case,
289 the CH_4 removal efficiency oscillations followed the same pattern as the temperature variations

290 at the top of the biofilter (40 cm; Figure 1). Nearly one month after the beginning of Sets B1 and
291 B2, RE values started to stabilize, averaging 16.3% (Biofilter B1), and 28.6% (Biofilter B2).

292 After 80 days (line-and-arrows in Figure 3), when the temperature of the system was high, a new
293 cooling cycle was started for Sets B1 and B2. Sets A1 and A2 were not subjected to such a slow
294 cycle. In Set B1, this resulted in a decrease in CH_4 removal efficiency that followed a pattern
295 similar to that of the temperature at the top of the biofilter (40 cm). After RE attained its
296 minimum value (26%) at Day 166, the CH_4 removal efficiency started to increase and the
297 packing bed media temperature at the base and mid-height of the biofilters reached a constant
298 value, whereas it continued to decrease at the top. At the end of the long cooling segment, the
299 value RE in Set B1 oscillated around 50%. As the system was warmed back again, efficiencies
300 increased to nearly 100%. Set B2 responded in a somewhat different way to the slow cooling
301 cycle. Indeed, the CH_4 removal efficiency oscillated rapidly between 50 and 100%, but
302 ultimately showed a decreasing pattern over time, reaching a minimum in the vicinity of 30%,
303 when the temperature at the top of the biofilter was below zero (~ -1.7 °C) and the temperature at
304 mid-height was at its lowest point (~ 11 °C) during this cooling cycle. Following an abrupt
305 warming of the system, efficiency values rapidly increased to almost 70%, where they remained
306 relatively stable, albeit with some oscillation. In summary, as far as cooling cycles for Sets B1
307 and B2 are concerned, the faster they were, the lower the CH_4 removal efficiencies. More
308 importantly, the results in Figure 3 showed that CH_4 removal efficiency is not only affected by
309 temperature, but also by the way in which the cooling-warming cycles were applied.

310 In Sets C1 and C2 (Figure 3), it was decided to apply cooling-warming cycles following a much
311 slower pace for both biofilters (Sets C1 and C2). Two complete cycles lasted 128 days. It can be
312 observed that both biofilters behaved in a quite similar manner, with CH_4 removal efficiencies

313 remaining very high (~100%) throughout the duration of Sets C1 and C2, i.e. even during
314 cooling cycles.

315 Temperature plays an important role in CH_4 removal efficiency. The exothermic reaction of CH_4
316 removal was maintained even during cold spells, simulated here by lowering the temperature of
317 the temperature-controlled bath and cooling system (Figure 1). Temperatures from the middle to
318 the bottom of the biofilters remained sufficiently high (Figure 3), with temperatures near the
319 bottom remaining nearly unchanged throughout the cycles, and temperatures at mid-height
320 decreasing by only a few degrees.

321 Another important factor to consider when analyzing the responses of the duplicate biofilters is
322 that 50% of the packing bed used in one set was reused to build the biofilters of the following
323 set. This, combined with the relatively stable temperatures at 5 and 20 cm and with the prolonged
324 testing periods of Sets A and B (that served as acclimatization for Set C), led to the nearly
325 constant efficiency (~ 100%) observed during Set C. If this behavior can be transposed to real
326 field conditions in dairy farms, biofilter efficiency to mitigate CH_4 emissions would be expected
327 to improve with time.

328 Table 2 summarizes several cases of application of the biofiltration technique to reduction of
329 CH_4 emissions. As far as biofiltration of exhaust air from animal houses is concerned, to our
330 knowledge, very few studies have been performed with inlet CH_4 concentrations as low as the
331 one considered herein (0.22 g m^{-3}; or 300 ppm), which reproduces conditions found during
332 winter in dairy farm barns, in Canada. Girard et al. (2011) loaded their biofilters with CH_4
333 concentrations varying from 0.16 to 2.8 g m^{-3} and obtained CH_4 removal efficiencies between 36
334 – 51%. Melse and Hol (2017) tested three different biofilters with loadings ranging from 0.001 to
335 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 ($K_{apparent}$) values indicated in Table 3 were used to determine biofilter volumes for winter conditions (V_{winter}).

Table 3 - Biofilter volumes representative of a regular-sized farm of 100 dairy cows during winter, according to the experimental sets.

359 Winter operating conditions may severely limit the activity of some methanotroph groups
360 (Gebert et al., 2003; Scheutz et al., 2009). Despite this fact, the $K_{apparent}$ values presented in Table
361 3 are somewhat closer to the K value of 7.5 h^{-1} found by Girard et al. (2011) for pig barn exhaust
362 air, and much higher than K values reported in the literature pertaining to biofiltration of CH_4 in
363 animal houses, i.e. K = 2 to 2.5 h^{-1} (Melse and Werf, 2005; Streese and Stegmann, 2003).

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

373

374 **4. Conclusions**

375 This paper addresses the use of biofiltration to mitigate CH_4 emissions under operating
376 conditions simulating those of dairy cow barns in Canada. The packing bed media used for the
377 laboratory biofilter (a mixture of commercial compost and straw) was selected based on the
378 highest oxidation rate. The CH_4 removal efficiency was affected by the temperature prevailing
379 within the biofilters, by the way in which the cooling-warming cycles were applied and by the
380 acclimatization process. As far as the latter, one important factor to consider was the fact that
381 part of the packing bed media used in one set was reused in subsequent biofilter tests of the

382 following set. The shorter the cooling-warming cycles, the more the oxidation rates varied. With
383 the longer cycles of the last set, which better simulate nature, CH_4 removal rates stabilized and
384 CH_4 removal efficiencies greatly improved, attaining nearly 100%.

385 The number of cows in dairy farms is estimated at 945,000 in Canada (Government of Canada,
386 2017b). Therefore, if the efficiencies obtained in this research can be transposed to real field
387 conditions, biofiltration would be able to abate from 2 x 10^6 and 3 x 10^6 t yr^{-1} of CO_2 equivalent
388 (USEPA, 2017).

389

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395

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Table 1 - CH_4 oxidation rates from the tested packing bed media.

Packing bed media[1]	Mixing ratio	Number of samples (n)	Average CH_4 oxidation rate ($\mu g\ CH4\ g_{dw}^{-1}\ h^{-1}$)	Min. – Max. ($\mu g\ CH4\ g_{dw}^{-1}\ h^{-1}$)	Standard deviation
comm-comp/swd/stw	1:1:1	11	0.74	0 – 1.15	0.36
comm-comp/stw	1:1	11	0.94	0.41 – 1.68	0.40
comm-comp/swd	1:1	11	0.75	0.32 – 1.00	0.23
comm-comp/swd	1:2	11	0.62	0.45 – 0.87	0.15
comm-comp/swd	2:1	11	0.85	0.38 – 1.41	0.29
man-comp/wd-chp	1:1	10	0.37	0 – 0.83	0.37
man-comp/wd-chp/stw	1:1:1	11	0.53	0 – 1.36	0.48

[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.

Working bed volume (L)	Packing media	Inlet CH_4 concentration (%v/v)	Inlet load (g CH_4 m^{-3} h^{-1})	EBRT (h)	CH_4 oxidation efficiency (%)	Monitoring time (days)	Temperature (°C)	Reference
5.85	Wood pine bark chips, perlite and compost (50:35:15)	0.17 – 0.18	15.6 – 16.0	0.073	36 – 51	100 – 250	18 – 22[1]	Gómez-Cuervo et al. (2016)
17.7	Stones	0.73	68.5	0.071	35	365	24[1]	Ramirez et al. (2012a)
18	Inorganic gravel material	0.3	20	0.1	70	N. Av	N. Av.	Veillette et al. (2012)
17.7	Inorganic gravel material	0.025 – 0.420	2.4 – 38.0	0.07	36 – 51	N. Av	20 – 25[1]	Girard et al. (2011)
2	Mature municipal solid waste compost	0.75 – 1.00	976 – 1,305	1.33	99 – 100	180	20 – 24[1]	Pawłowska et al. (2011)
17.5	Cylindrical pieces of an inorganic gravel material	0.13 – 0.98 0.26 – 1.18 0.19 – 1.03 0.13 – 0.96	3.0 – 22.4 11.9 – 54.0 13.1 – 70.7 16.4 – 129.5	0.292 0.145 0.097 0.053	94 – 100 88 – 91 82 – 88 47 – 60	30	20 – 26[1]	Nikiema and Heitz (2009)
18	Cylindrical pieces of an inorganic gravel material	0.13 – 1.00	12 – 95	0.072	50 – 37	19	N. Av	Nikiema et al. (2009)
160	Expanded perlite and garden compost (40:60)	0.075 – 0.850	0.1 – 25.0	0.12 – 1.33	85 – 18	60	4.7 – 21.1[2]	Melse and Werf (2005)
17,000 47,000 110,000	Wood chip	0.00032 0.0031 0.0117	N. Av	0.0004 0.0007 0.001	N. D.	180 – 365	15 – 22[2] 23 – 25[2] 22 – 23[2]	Melse and Hol (2017)
7.85	Composted leaves and sponge-based material Composted leaves and blast furnace slag Composted leaves and expanded vermiculite	0.17 – 3.6	3.0 – 148.8	0.12 – 0.71	4 – 56 4 – 54 13 – 95	188	19 – 36[1]	Brandt et al. (2016)

[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.

	$K_{apparent}$ (h^{-1})	V_{winter} (m^3)
Set A1	4.6	1168.7
Set A2	3.0	914.6
Set B1	1.9	1598.8
Set B2	3.2	1232.3
Set C1	17.5	837.1
Set C2	12.7	996.1

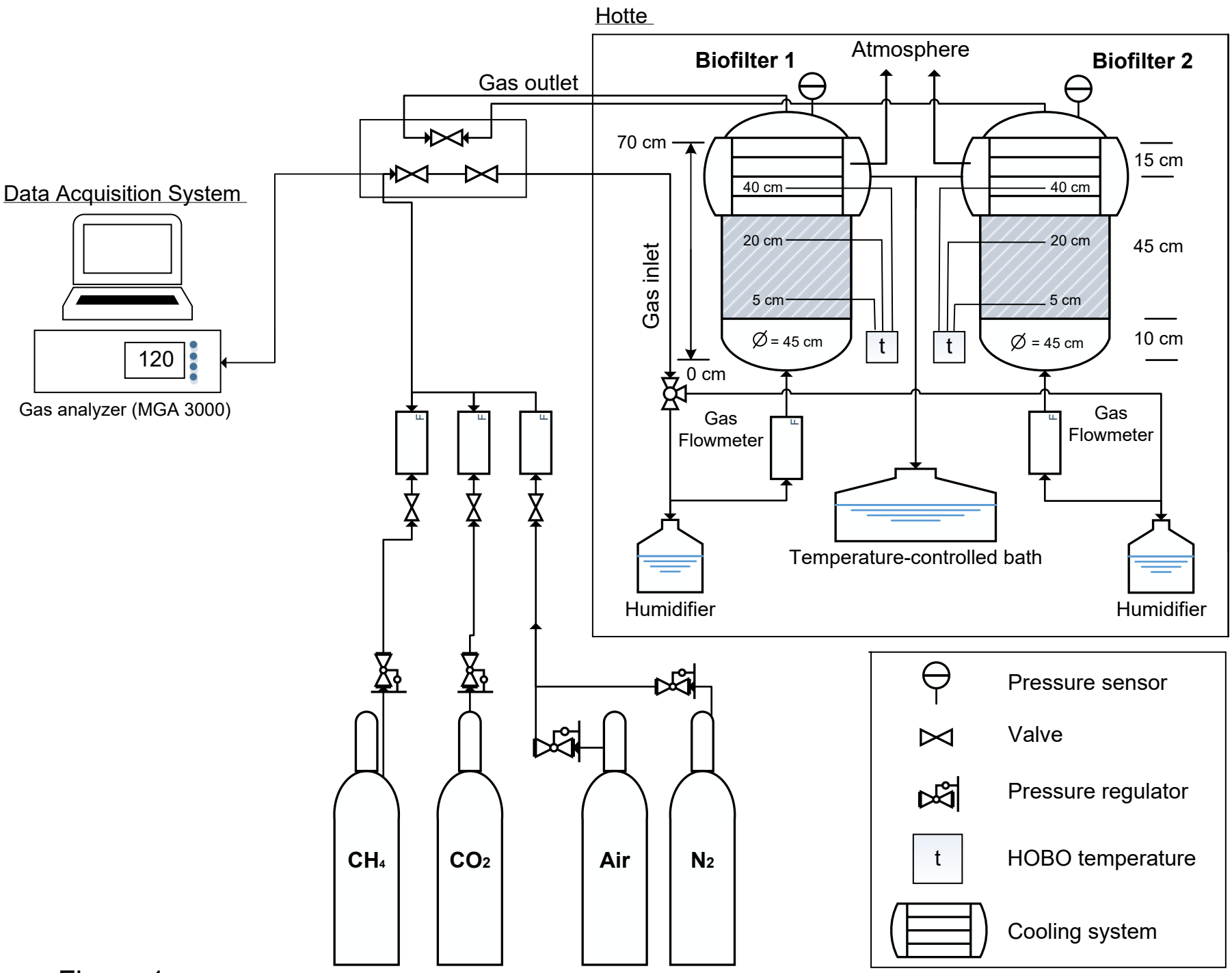
Hotte
Biofilter 1
Atmosphere
Biofilter 2
Gas outlet
Data Acquisition System
70 cm
40 cm
40 cm
15 cm
20 cm
20 cm
45 cm
5 cm
5 cm
Gas inlet
∅ = 45 cm
∅ = 45 cm
t
t
10 cm
120
0 cm
Gas analyzer (MGA 3000)
Gas Flowmeter
Gas Flowmeter
Temperature-controlled bath
Humidifier
Humidifier
CH4
CO2
Air
N2
Pressure sensor
Valve
Pressure regulator
t
HOBO temperature
Cooling system

Figure 1

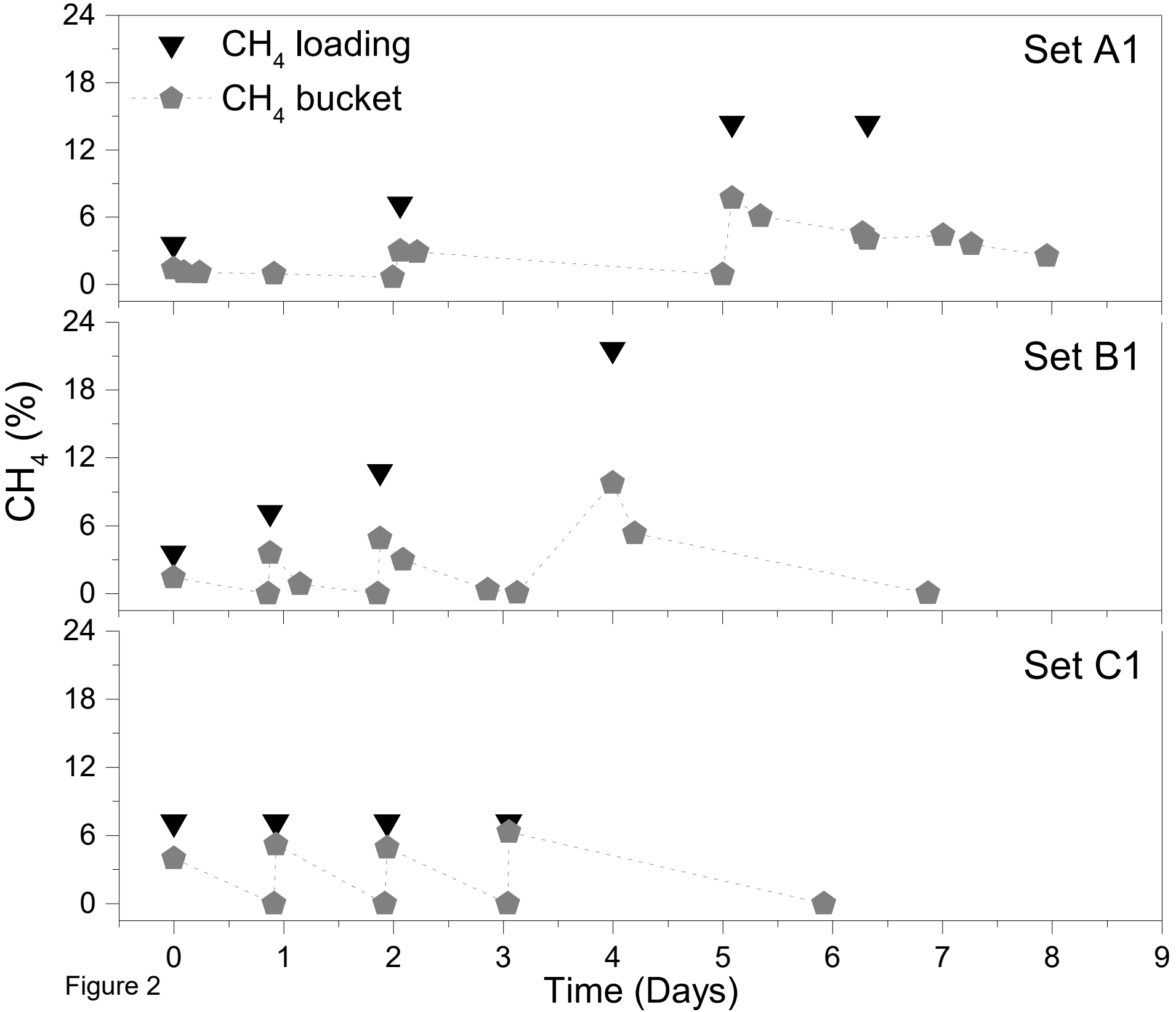
CH4 loading
CH4 bucket
Set A1
Set B1
Set C1
CH4 (%)
Time (Days)
0
6
12
18
24
0
1
2
3
4
5
6
7
8
9

Figure 2

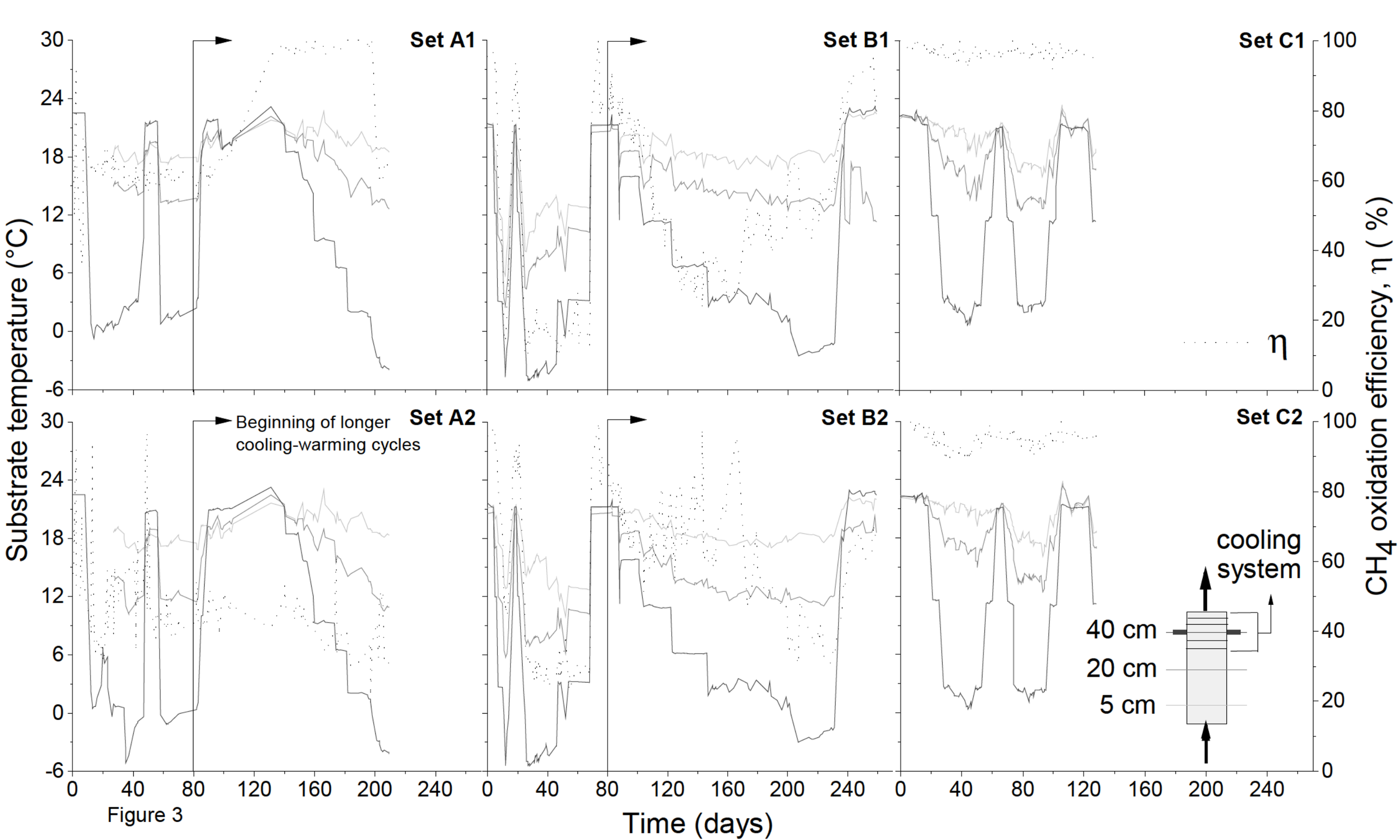
Set A1
Set B1
Set C1
Set A2
Set B2
Set C2
Beginning of longer
cooling-warming cycles
Substrate temperature (°C)
CH4 oxidation efficiency, η (%)
η
cooling
system
40 cm
20 cm
5 cm
Time (days)
30
24
18
12
6
0
-6
100
80
60
40
20
0
0
40
80
120
160
200
240

Figure 3